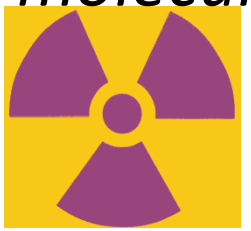
Chapter 2
Basic Spectrometric Methods (光譜法)

References:

- Skoog, D.A., Holler, F.J., Crouch, S.R. (2007). Principles of Instrumental Analysis, 6th edition, Thomson, Chapters 6, 7 & 13.
- Skoog, D.A., Crouch, S.R., Holler, F.J., West, D.M. (2014). Fundamentals of Analytical Chemistry, 9th edition, Brooks/Cole, Chapters 24 & 25.

Basic Spectrometric Methods

- Spectrometry(光譜法): The measurement of electromagnetic radiation as a means of obtaining information about physical systems and their components
- Spectroscopy (光譜學): science studies the interactions of radiation with matter (*composed of atoms and molecules*)



Classification of spectrometric techniques

- Atomic spectroscopy (原子光譜學):
  - Atomic absorption spectrometry (原子吸收光譜法)
  - Atomic emission spectrometry (原子發射光譜法)
  - Atomic fluorescence spectrometry (原子熒光光譜法)
  - Atomic mass spectrometry (原子質譜法)
  - Atomic x-ray spectrometry (原子x-射線光譜法)

Classification of spectrometric techniques

- Molecular spectroscopy (分子光譜學):
  - UV/VIS absorption spectrometry (紫外及可見光吸收光譜法)
  - Infrared absorption spectrometry (紅外光吸收光譜法)
  - Luminescence spectrometry (冷光光譜法)
  - Raman spectrometry (拉曼光譜法)
  - NMR spectrometry (核磁共振光譜法)
  - Mass spectrometry, Emission spectrometry, X-ray spectrometry

Nature of interaction

- Absorption (吸光):

Radiation absorbed by matter
Totally absorbed- black in colour

Nature of interaction

- Reflection (反射):

Energy

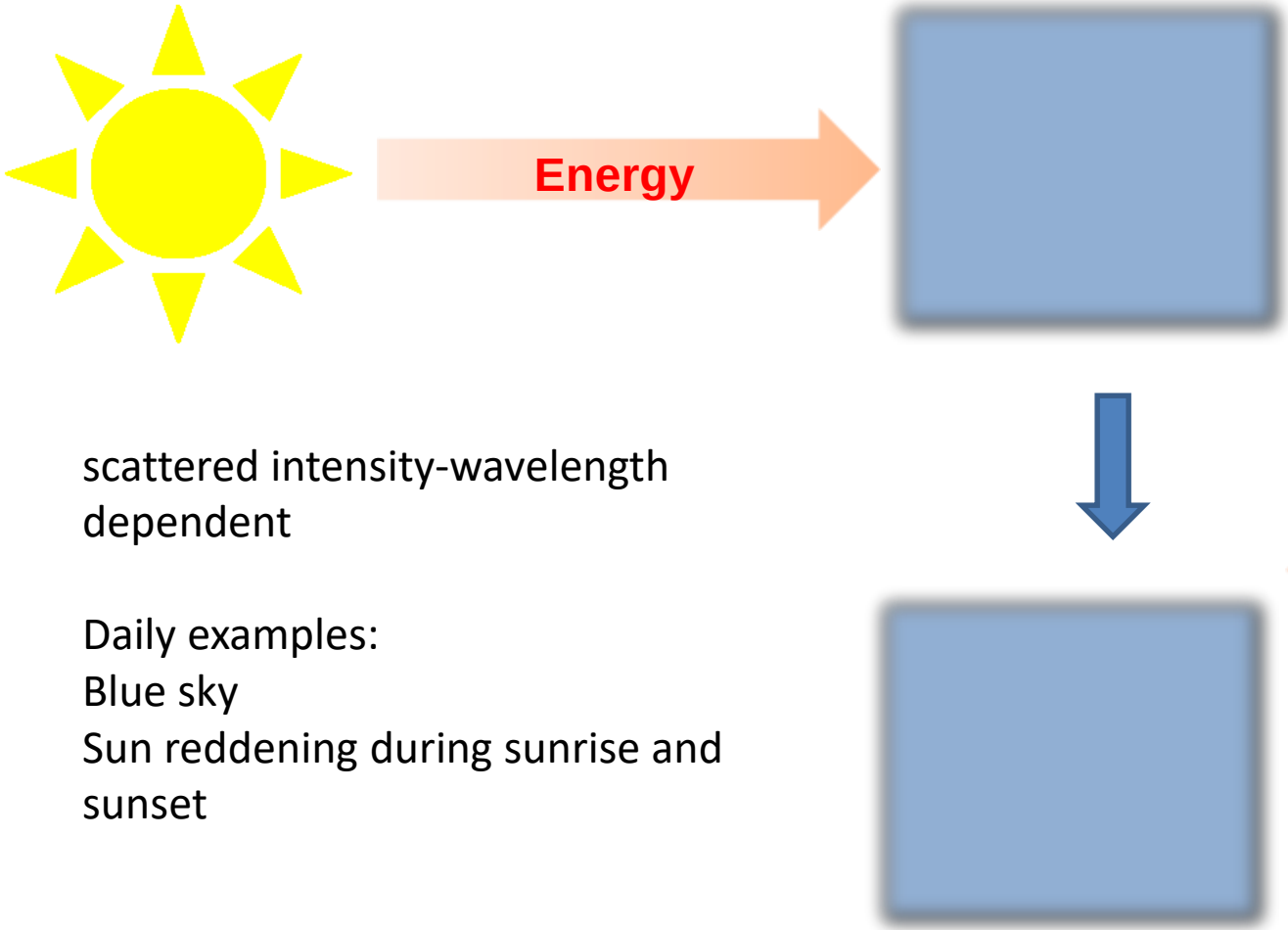
Partially absorbed and reflected

The colour of an object is the result of part of visible light absorbed and then part of visible light reflected by it.

IVE

Nature of interaction

- Scattering (散射):



scattered intensity-wavelength dependent

Daily examples:
Blue sky
Sun reddening during sunrise and sunset

Introduction to Spectroscopy

2 steps in light/matter interactions:

- **Absorption:**
  - During light absorption, electrons in atoms/molecules will be excited (激發)

- **Relaxation:**
  - By emitting radiation(*after absorption of energy / radiation*), electrons of atoms/molecules would change from its excited state(激態) to ground state(基態)

Introduction to Spectrometry

Two kind of analysis:

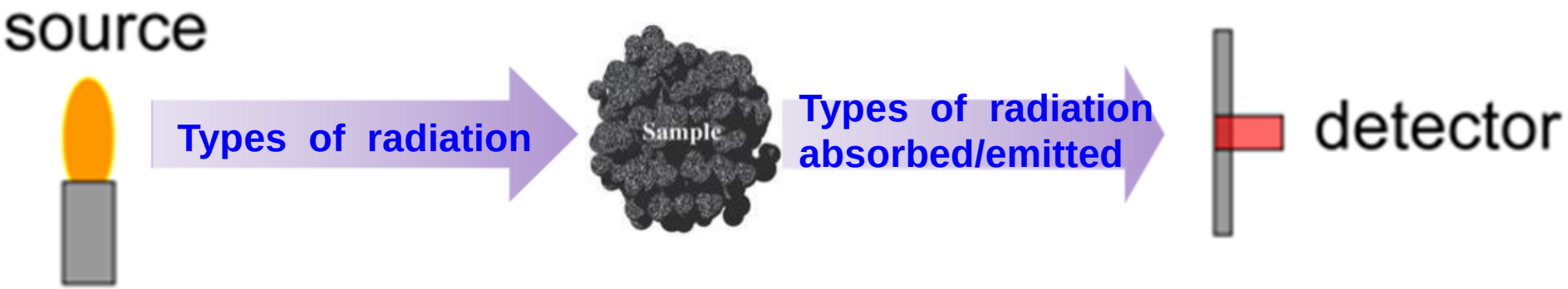
- **Qualitative analysis(定性分析)**
  - Want to know what is in our sample

- **Quantitative analysis(定量分析)**
  - Want to know how much of a particular chemical species is in our sample

Introduction to Spectrometry

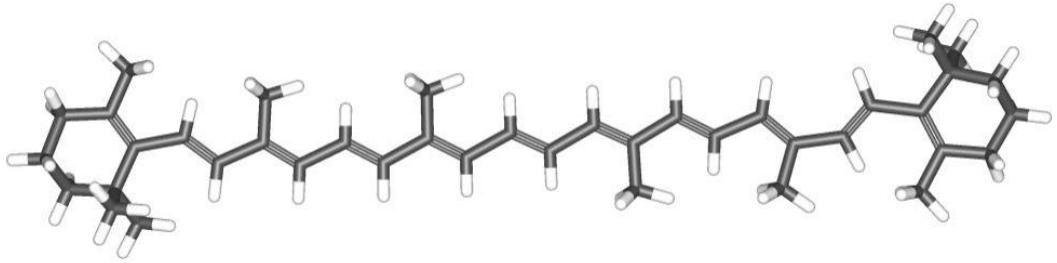
Qualitative analysis by spectrometry:

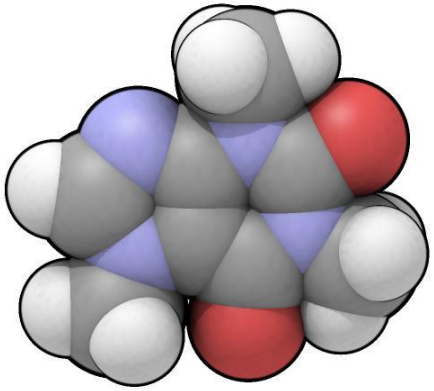
Upon energy irradiation to the sample, the type of chemical species in the sample is obtained by measuring the intensity(強度) of energy **absorbed**(in absorption spectroscopy) **or emitted**(in emission spectroscopy).



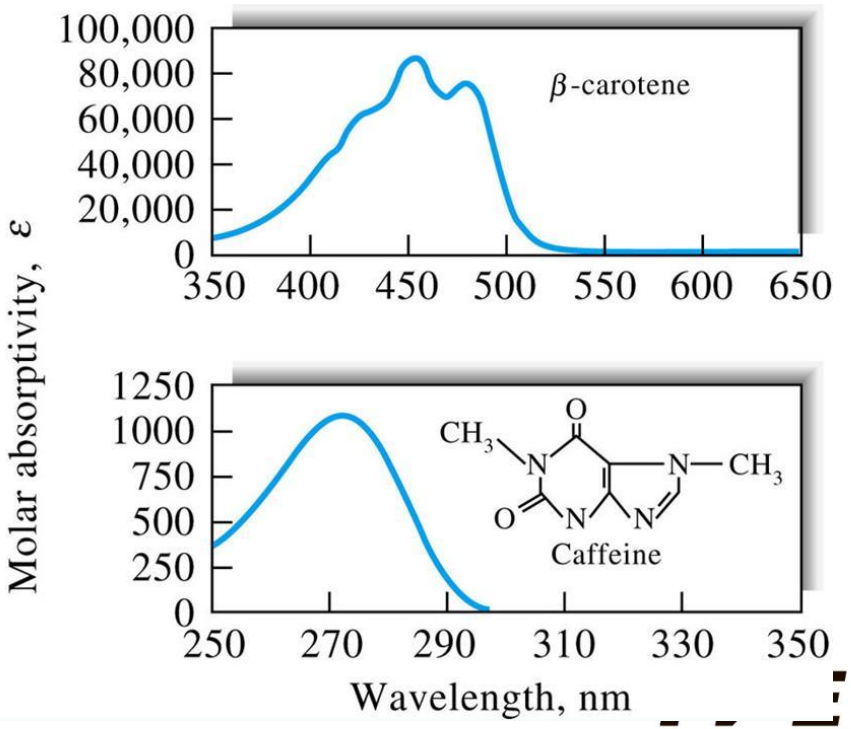
Introduction to Spectrometry

Qualitative analysis : a measurement of the peak position of radiation by an electronic device



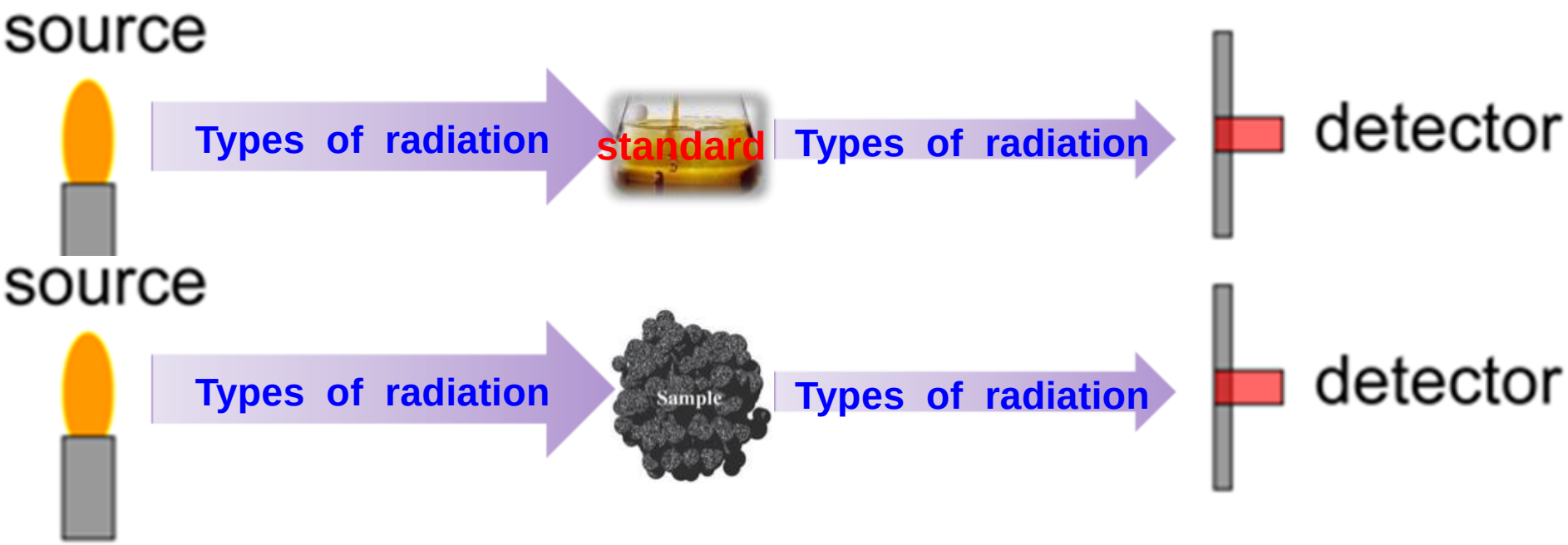


Spectrum (光譜)



Introduction to Spectrometry

Qualitative analysis:

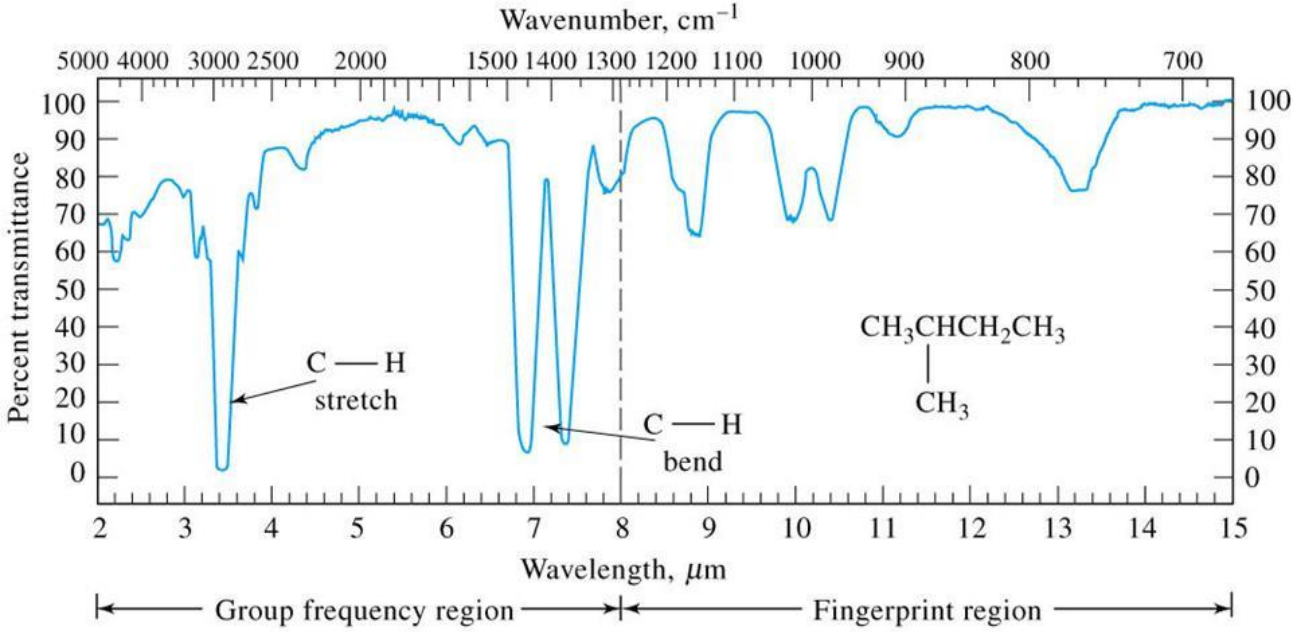


We have to build up a library of database before identifying the unknown sample.

Introduction to Spectrometry

Qualitative analysis:

⇒ structural determination

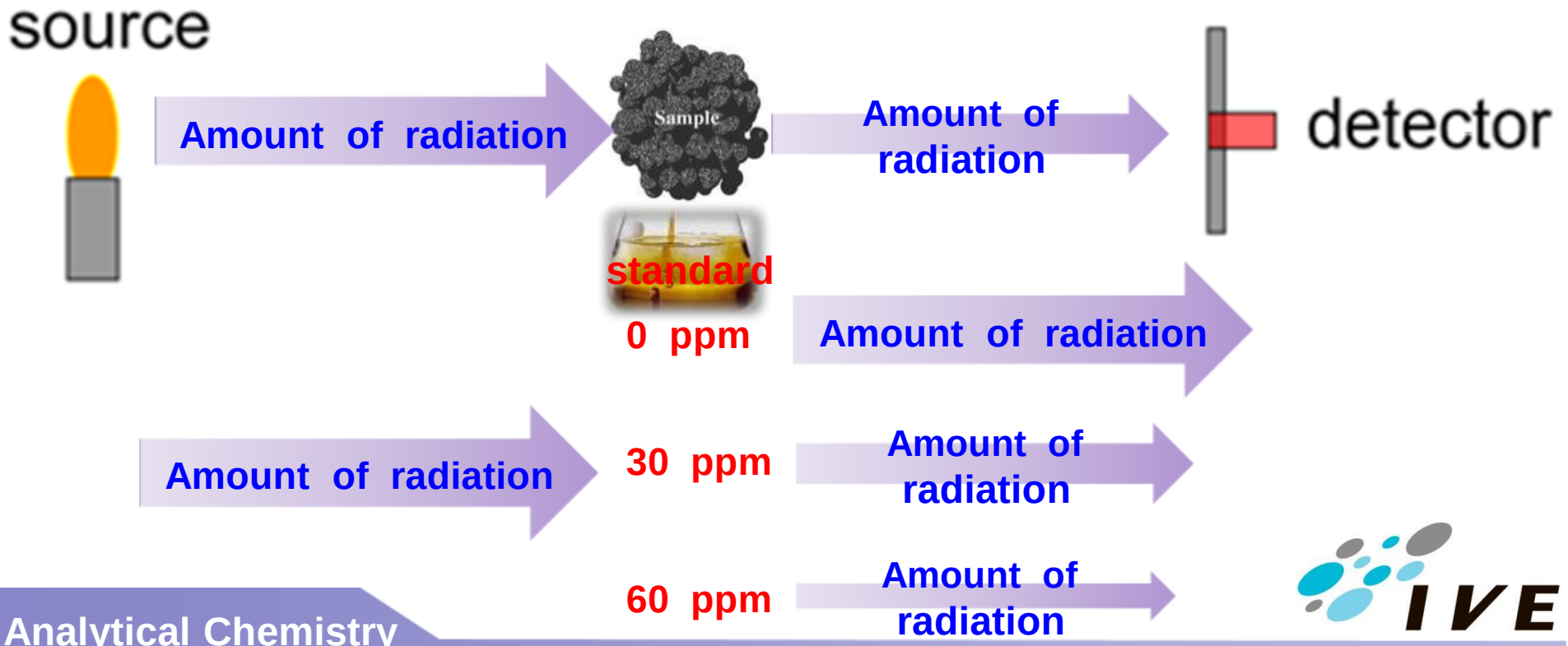


In real applications, more than one technique is needed for verification of one unknown molecule/compound.

Introduction to Spectrometry

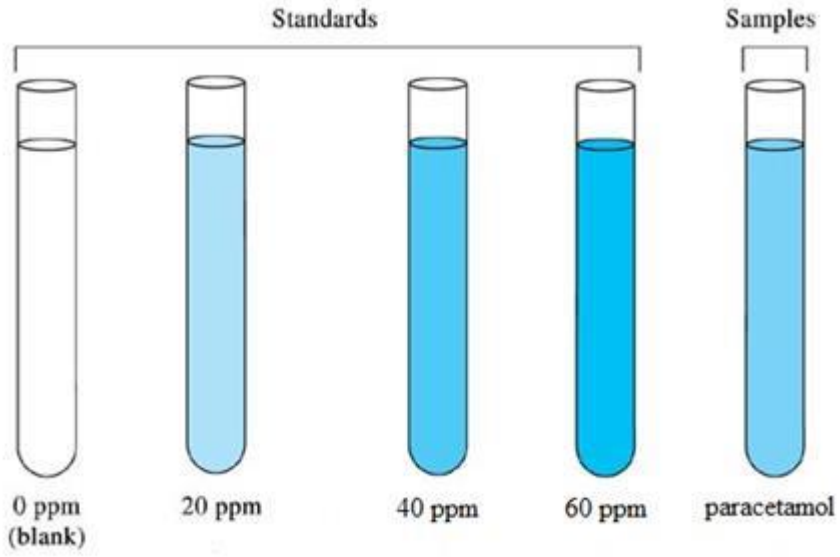
Quantitative analysis by spectrometry (光譜法): :

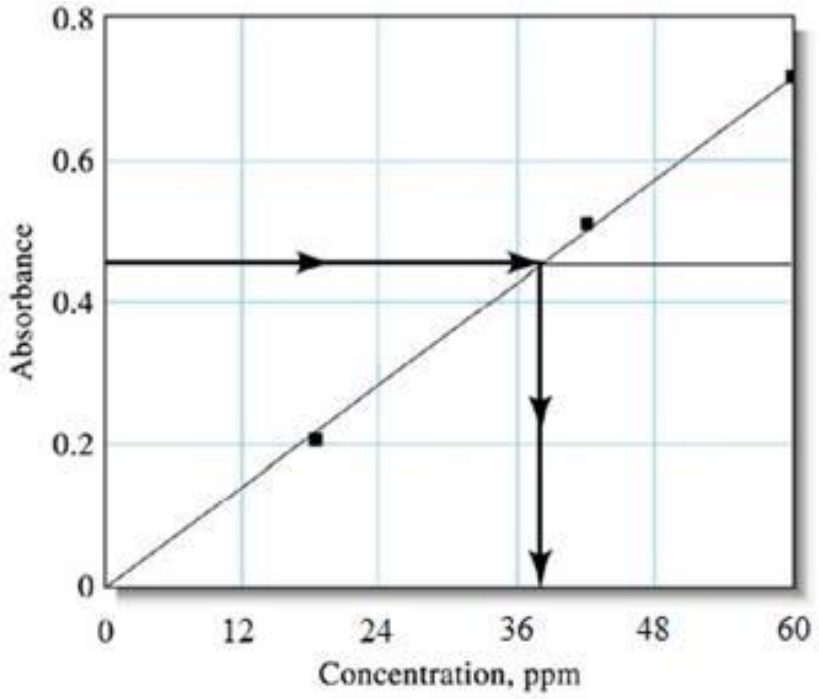
From the amount of radiation or energy absorbed/ emitted, the amount of material present can be evaluated.



Introduction to Spectrometry

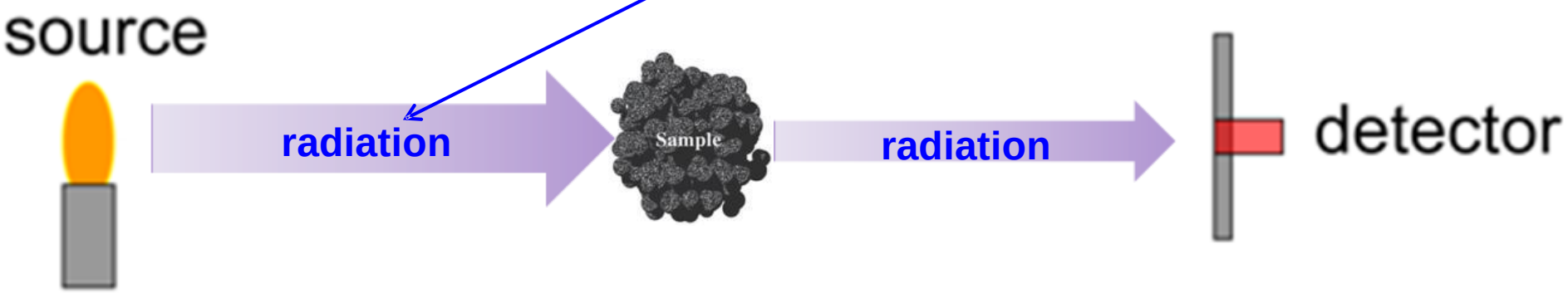
Spectrometry (光譜法): a measurement of the intensity (強度) of radiation by an electronic device for **quantitative analysis**





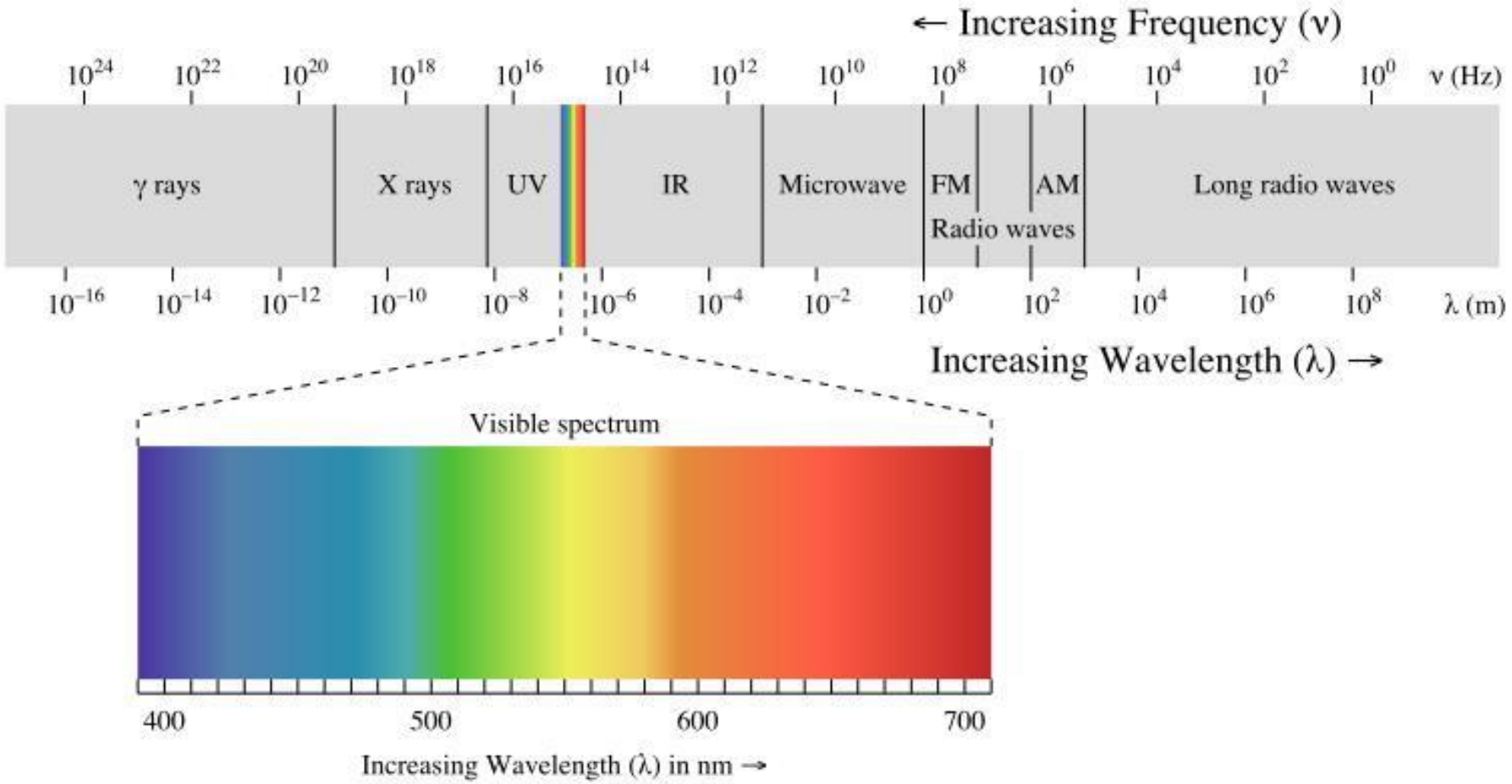
Electromagnetic radiation (電磁輻射)

- Spectrometric methods: based on the interaction of **electromagnetic (EM) radiation** and matter



Electromagnetic radiation (電磁輻射)

The electromagnetic (EM) spectrum

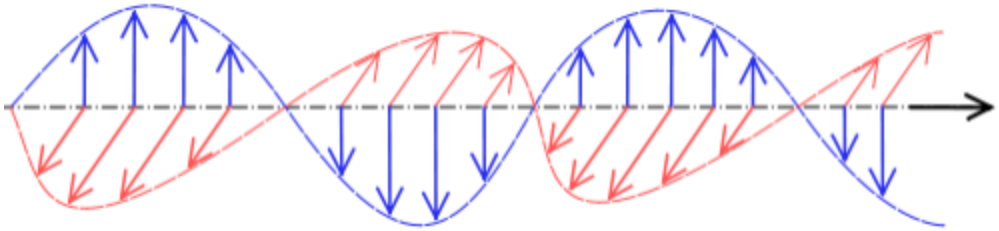


Electromagnetic radiation (電磁輻射)

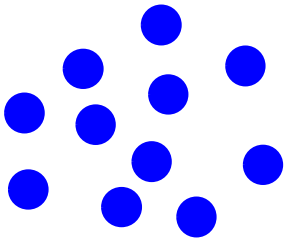
Properties of electromagnetic radiation

Properties of EM radiation is described by both wave and particle (粒子) models. This phenomenon is called **wave–particle duality(波粒二象性).**

Wave model



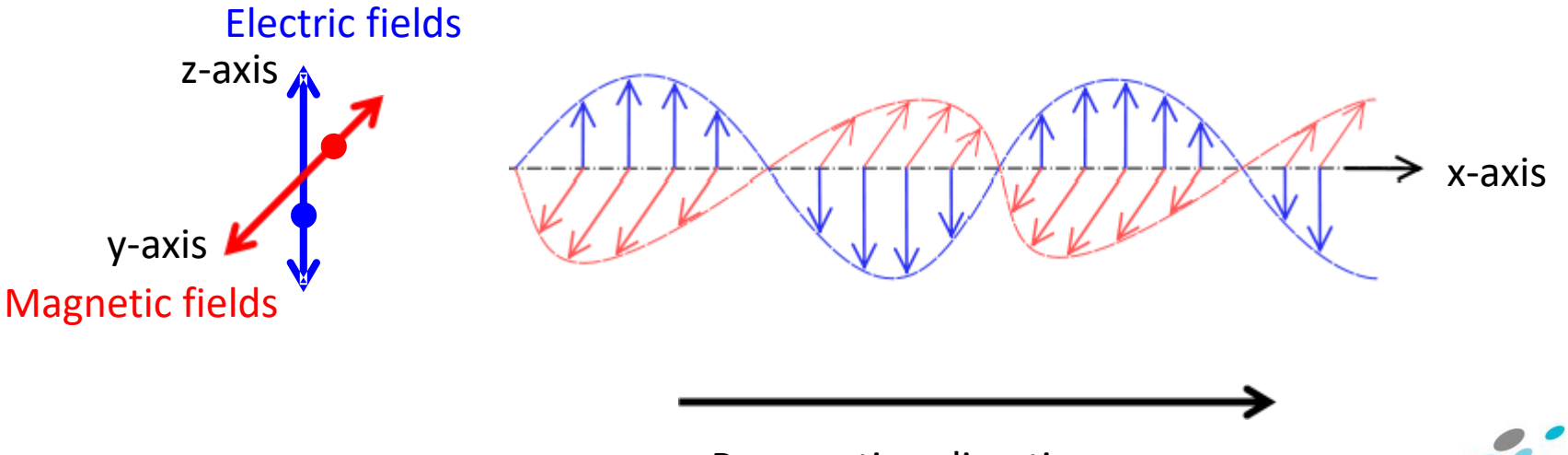
Particle model



Electromagnetic radiation (電磁輻射)

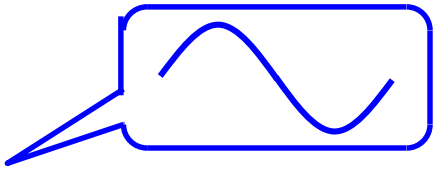
Wave model

- Electromagnetic waves(電磁波) are oscillations of electric and magnetic fields that propagate at the speed of light through a vacuum.
- It can travel through vacuum and requires no supporting medium(媒介)

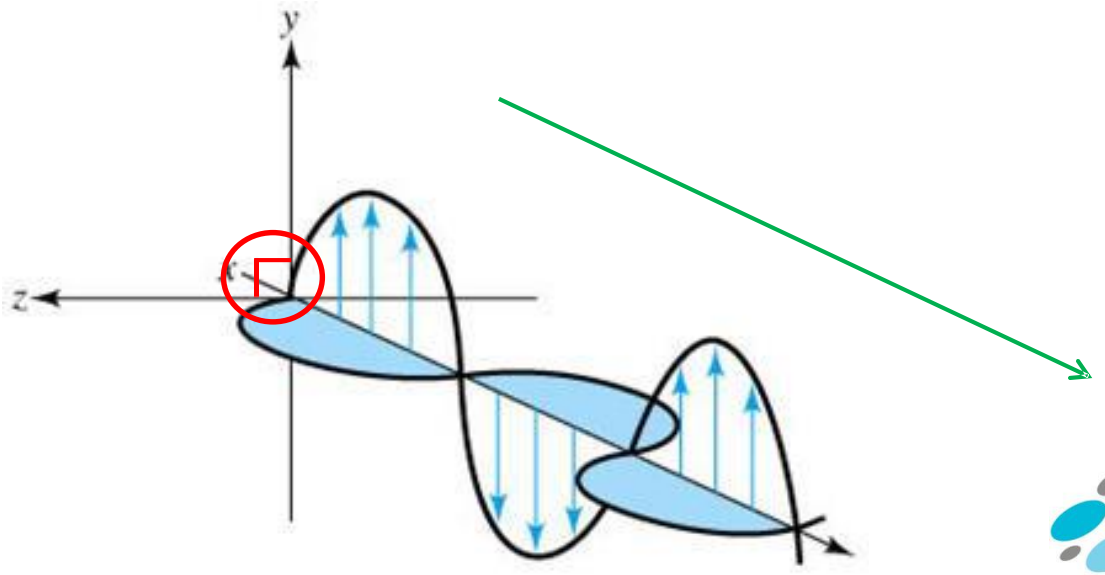


Electromagnetic radiation (電磁輻射)

- For wave model, electric field(電場)
  + magnetic fields (磁場)

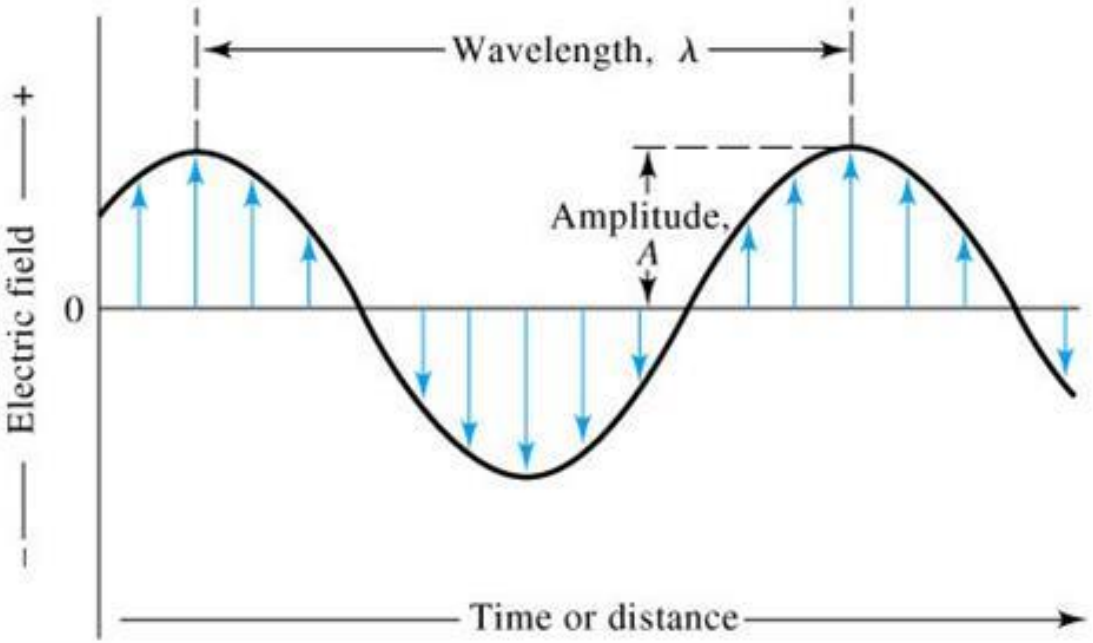


- in phase
- sinusoidal oscillations (正弦振動) at right angle to each other and to the direction of propagation (傳播)



Electromagnetic radiation (電磁輻射)

- For wave model, characteristics described by:
  - wavelength (波長)
  - frequency (頻率)
  - velocity (速率)
  - amplitude (振幅)
  - period, p (週期)



Electromagnetic radiation (電磁輻射)

- For wave model,

Red: 4.3×10^{14} Hz
Yellow: 5.45×10^{14} Hz
Blue: 7.5×10^{14} Hz

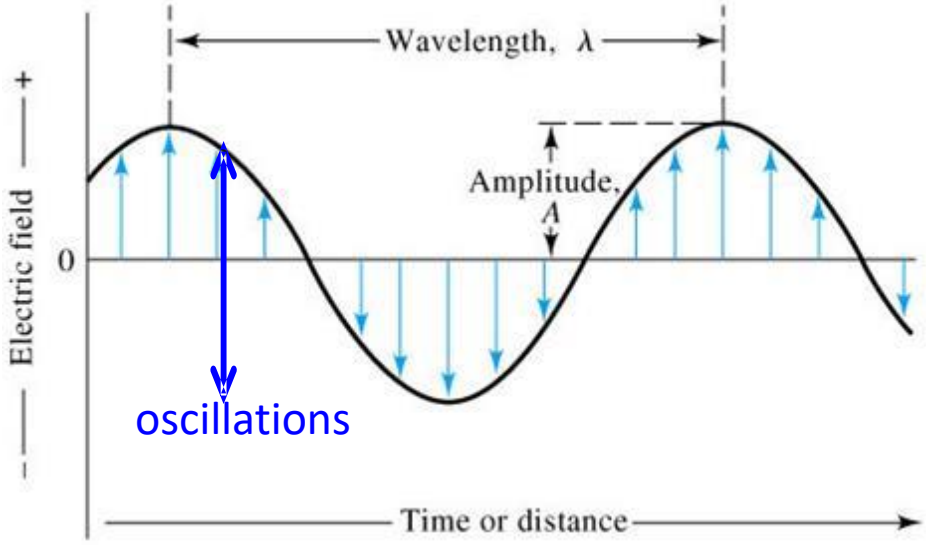
➢ Frequency (ν):

number of oscillations of the field thatoccur per second

➢ Period (p):

length of time(number of seconds) of the field taken in one oscillation

=> ν(Hz) = 1/ p(s)



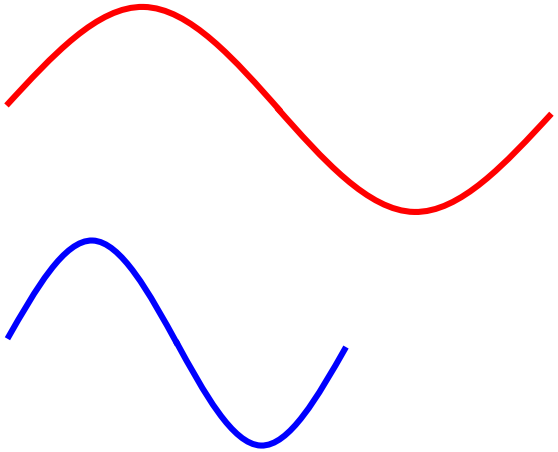
Electromagnetic radiation (電磁輻射)

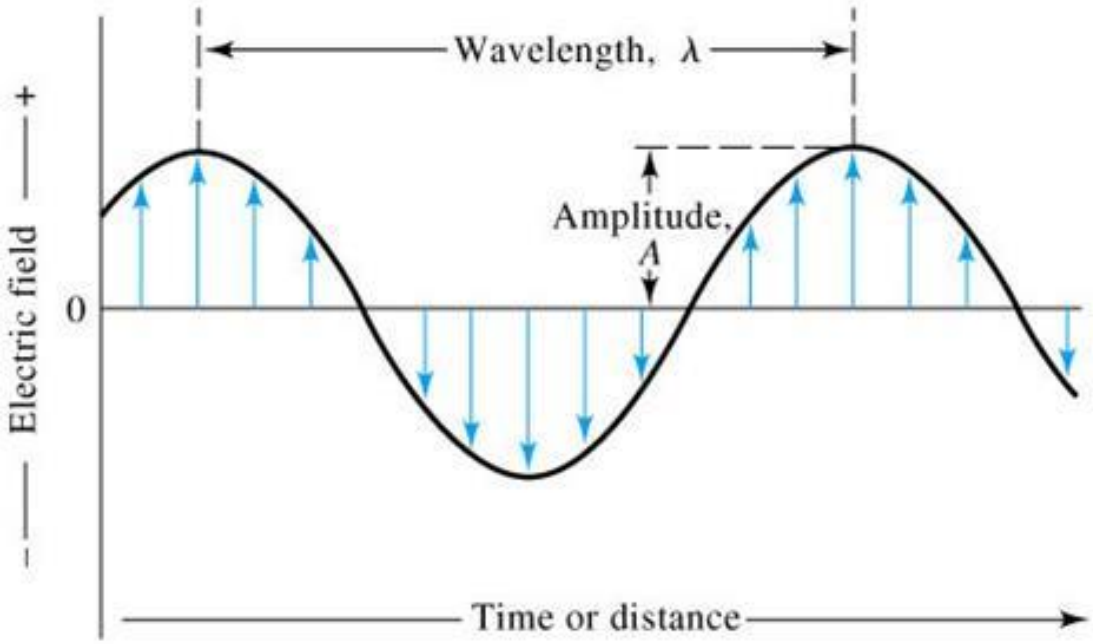
For wave model,

- Wavelength (λ):

Red: 700 nm
Yellow: 550 nm
Blue: 400 nm

- linear distance between any two equivalent points on successive waves





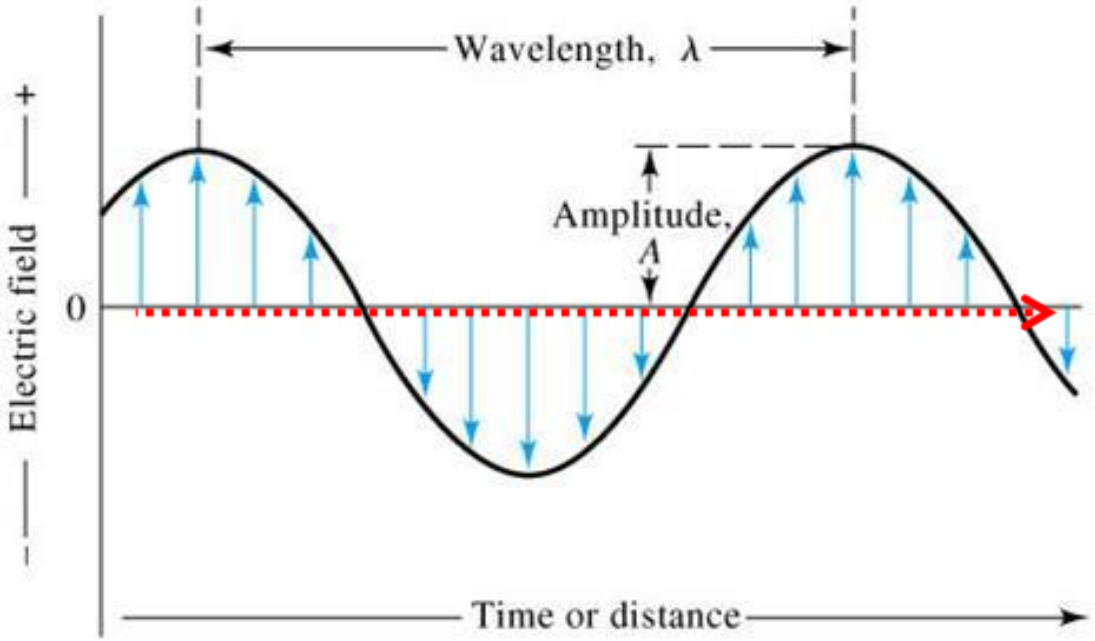
Electromagnetic radiation (電磁輻射)

- For wave model,

➢ Velocity of propagation (v):

- depends upon the composition of the medium which it passes

$v = \nu\lambda$



Electromagnetic radiation (電磁輻射)

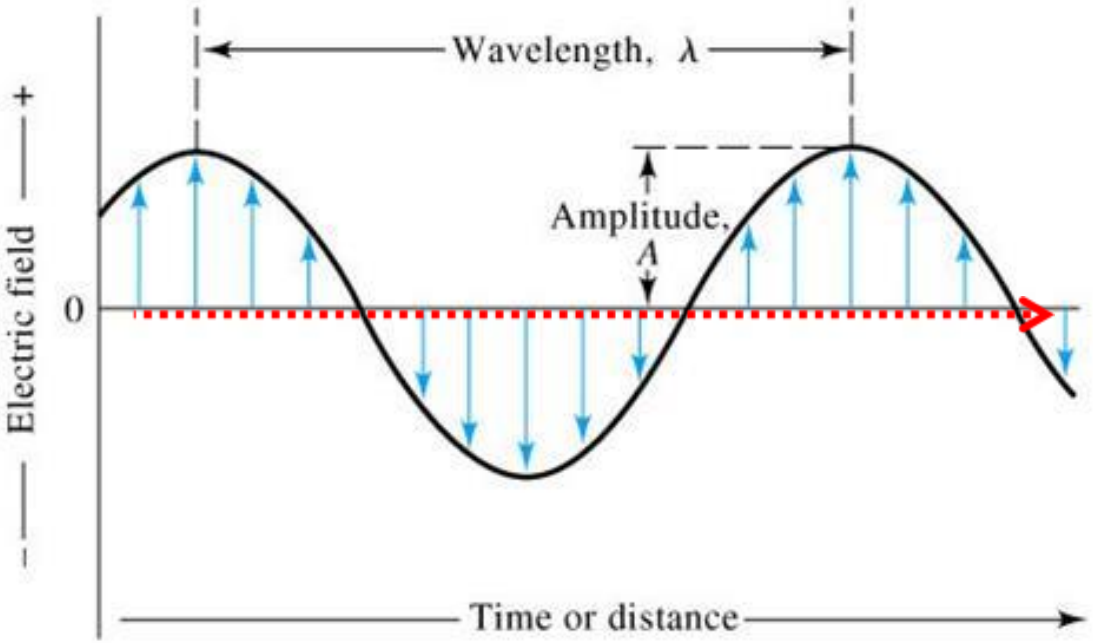
Properties of electromagnetic radiation

In case of vacuum(真空),

Velocity of propagation, v

= 2.99792 x 10^8 ms^{-1}

Velocity of light in air decreased by 0.03%



Electromagnetic radiation (電磁輻射)

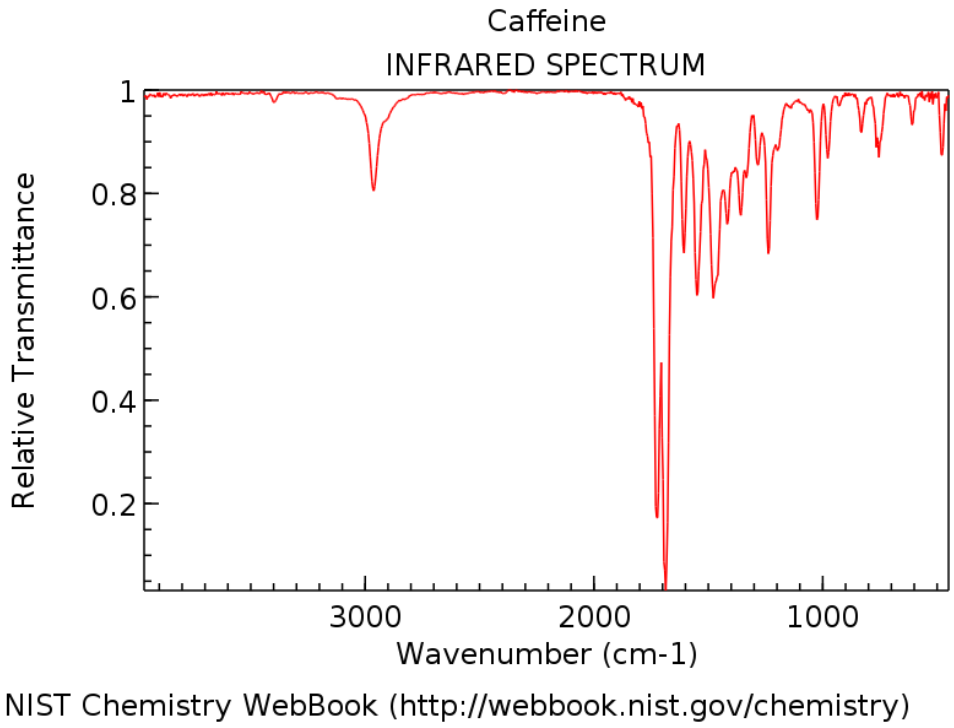
Properties of electromagnetic radiation

- For wave model,
  - Wavenumber (波數) ($\bar{\nu}$):

    $= 1/\lambda$

    Since $v = \nu\lambda$,

    $1/\lambda = \nu / v$

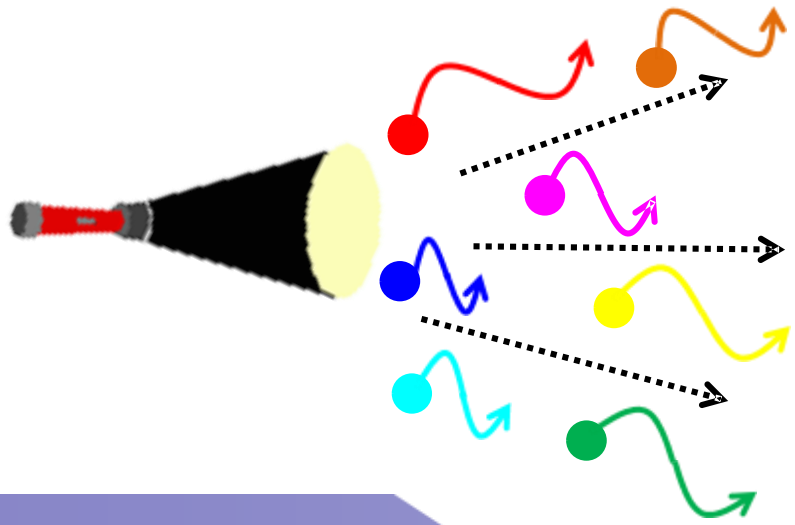


Electromagnetic radiation (電磁輻射)

Particle model

EM radiation can also be viewed as:

- a stream of discrete (不連續的) particles
- wave packets of energy called photons (光子)

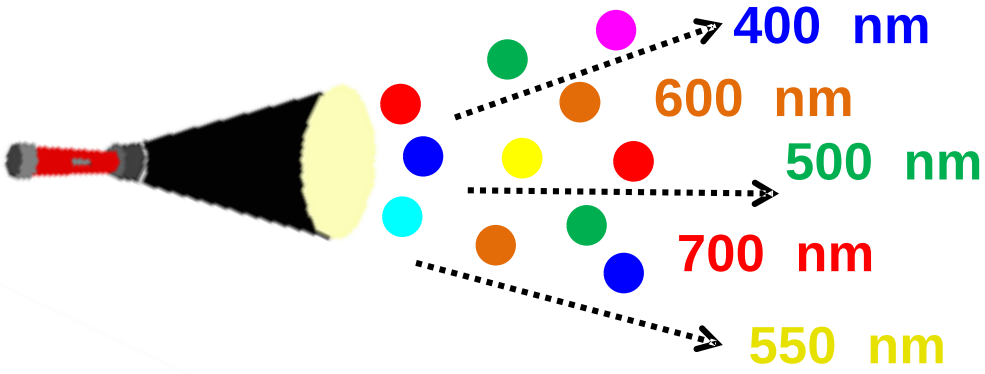


Electromagnetic radiation (電磁輻射)

Properties of electromagnetic radiation

The energy of the photon is:

$$E = h\nu = hc / \lambda$$



h = Planck's constant = 6.6254×10^{-34} joule second

c = the speed of light = $\nu\lambda = 2.99792 \times 10^{8}$ ms^{-1}

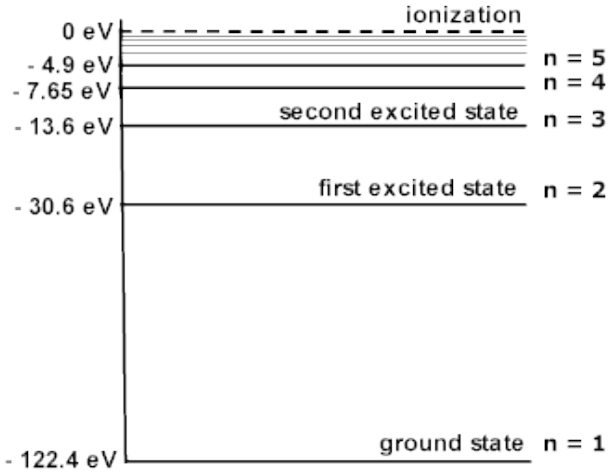
Electromagnetic radiation (電磁輻射)

Properties of electromagnetic radiation

- For particle model,

➢ Electron in the ground state absorbs photon and re-emits it

➢ energy transfer (interaction of photon and electrons)



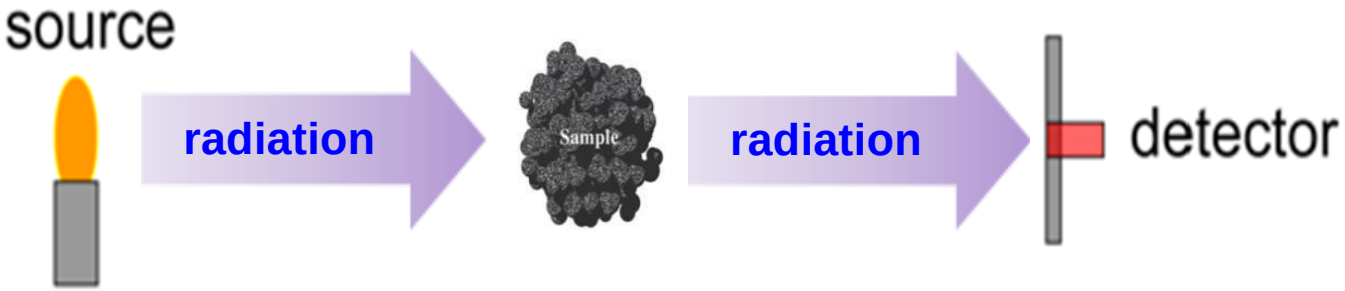
The electron inside atom/molecule is excited between energy levels(能階) according to the energy of the photon.

Classification of spectrometric techniques

- Based on types of spectrometry (光譜法):

  1. Absorption spectrometry (吸收光譜法)

  Measure radiation absorbed by the matter

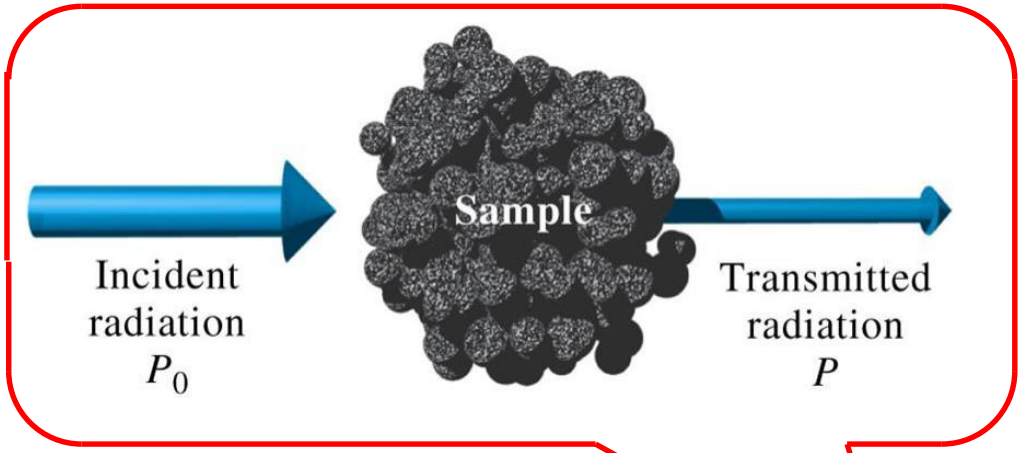


In this kind of spectrometry, the energy of the radiation would be absorbed by the sample and only part of the radiation(of same wavelength) remained is detected.

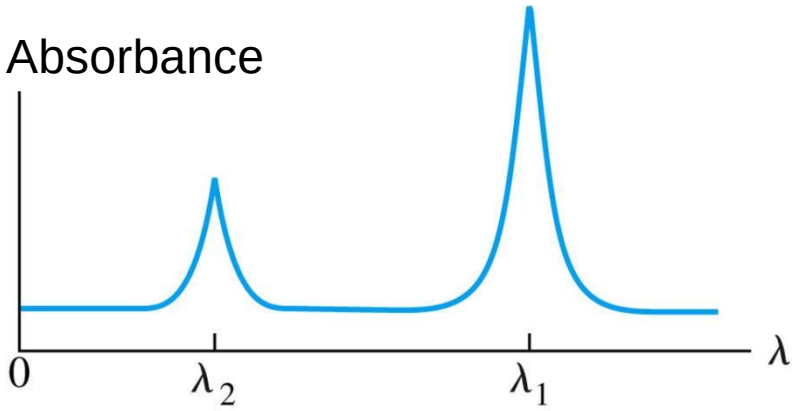
Classification of spectrometric techniques

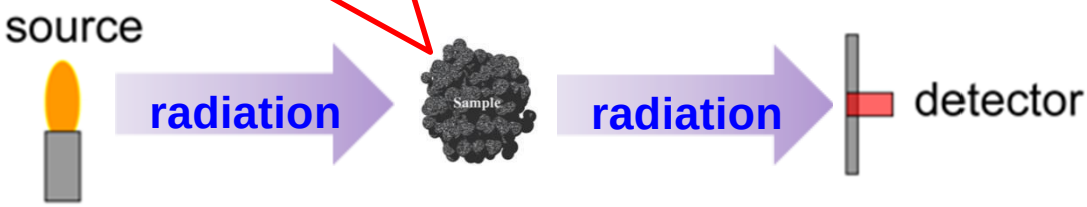
- Based on types of spectrometry (光譜法):

  Absorption spectrometry (吸收光譜法)



Po, P refer to intensity



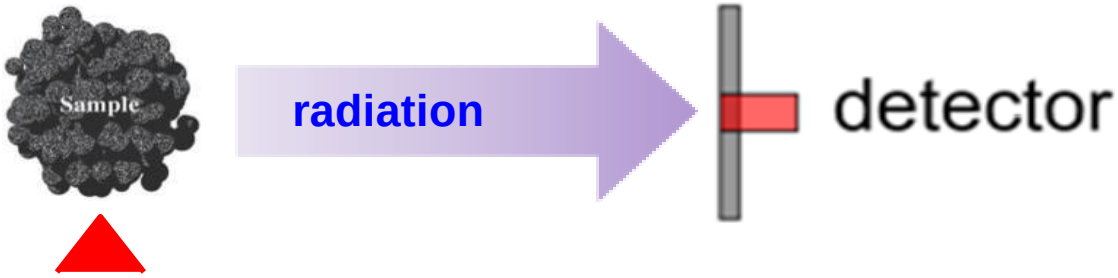


Classification of spectrometric techniques

- Based on types of spectrometry (光譜法):

  2. Emission spectrometry (放射光譜法)

- Measure the radiation being emitted by the matter

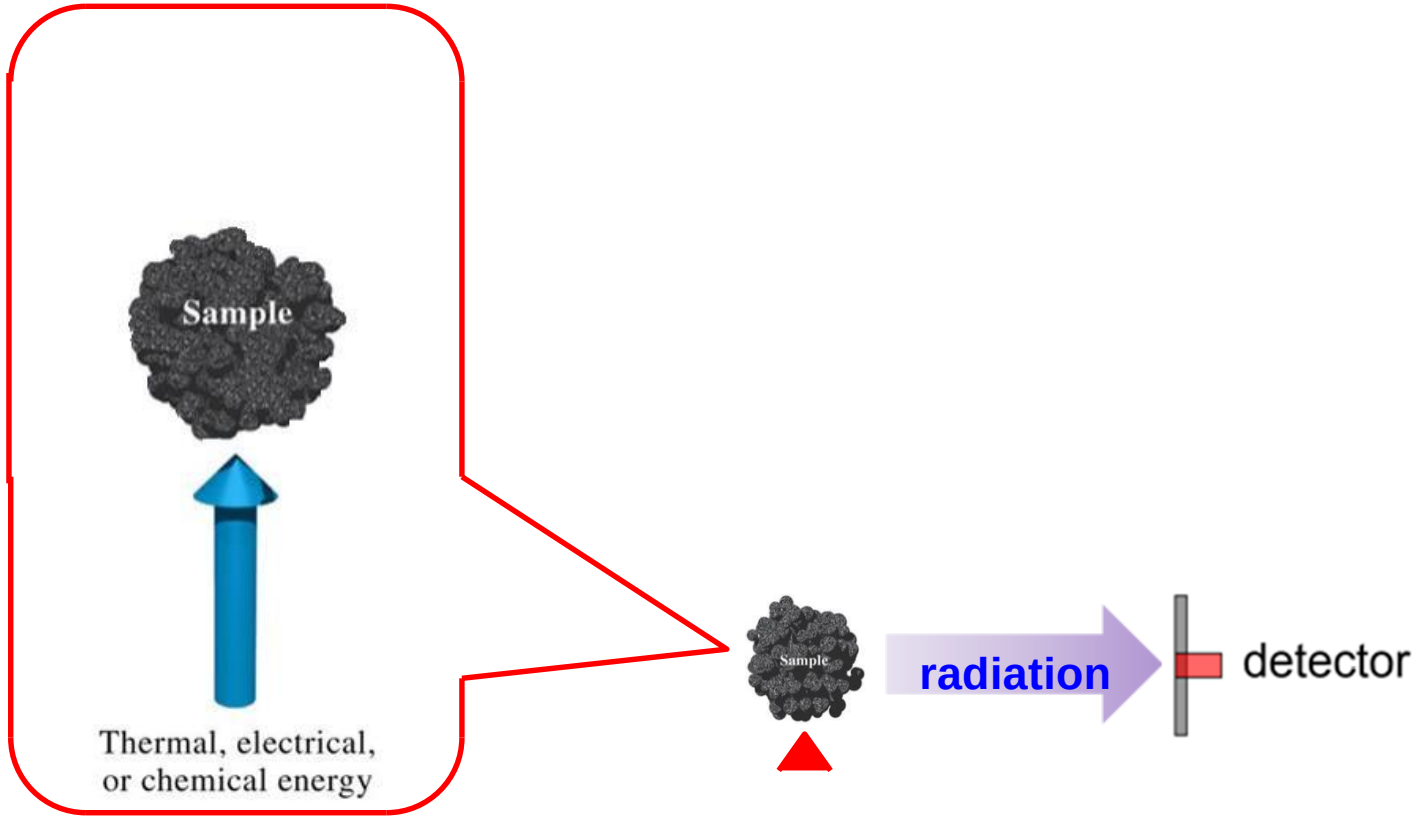


In this type of spectrometry, the sample absorbs the radiation/energy and then emit radiation of different wavelength.

Classification of spectrometric techniques

- Based on types of spectrometry (光譜法):

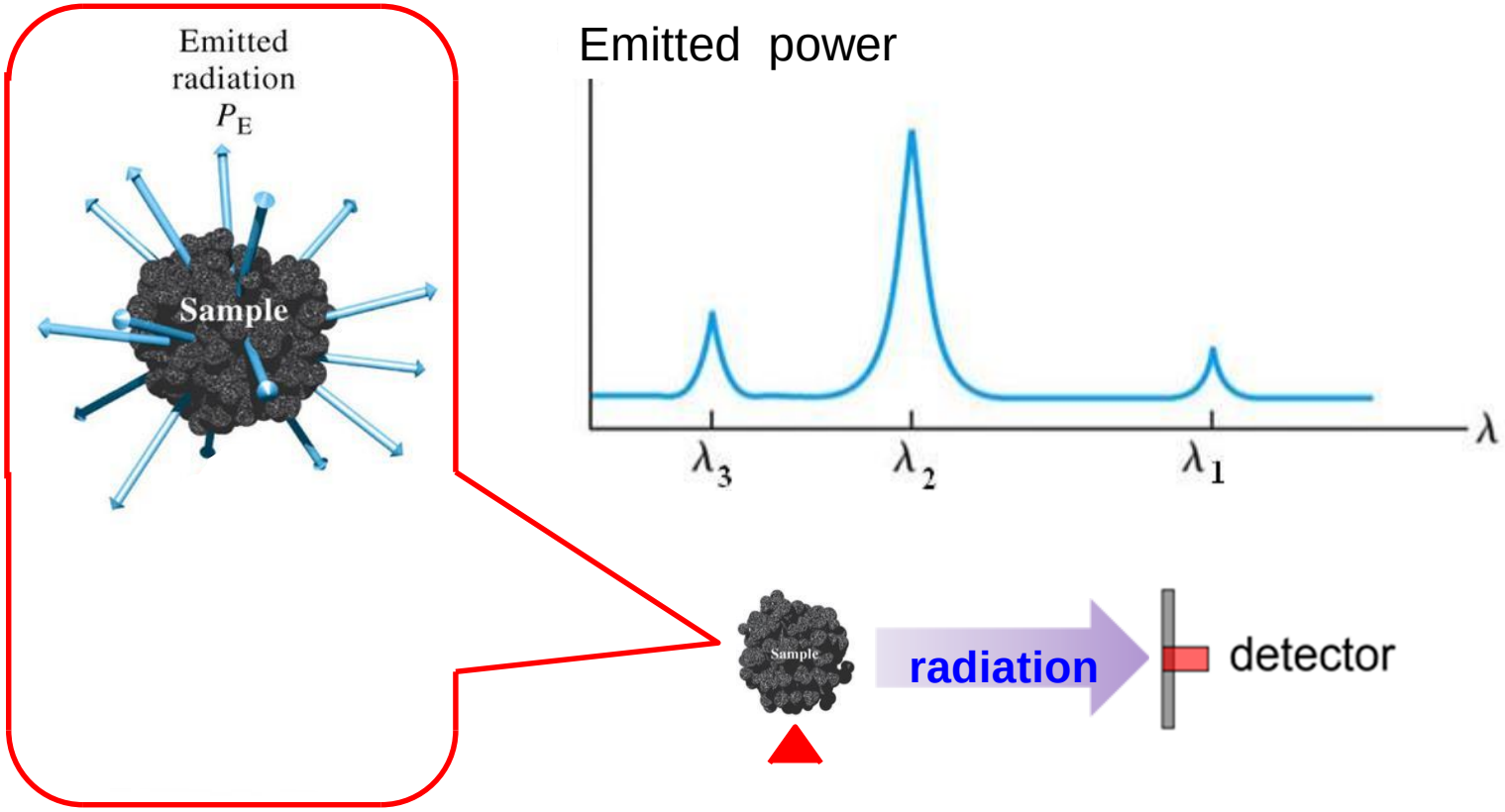
➢ Emission spectrometry (放射光譜法)



Classification of spectrometric techniques

- Based on types of spectrometry (光譜法):

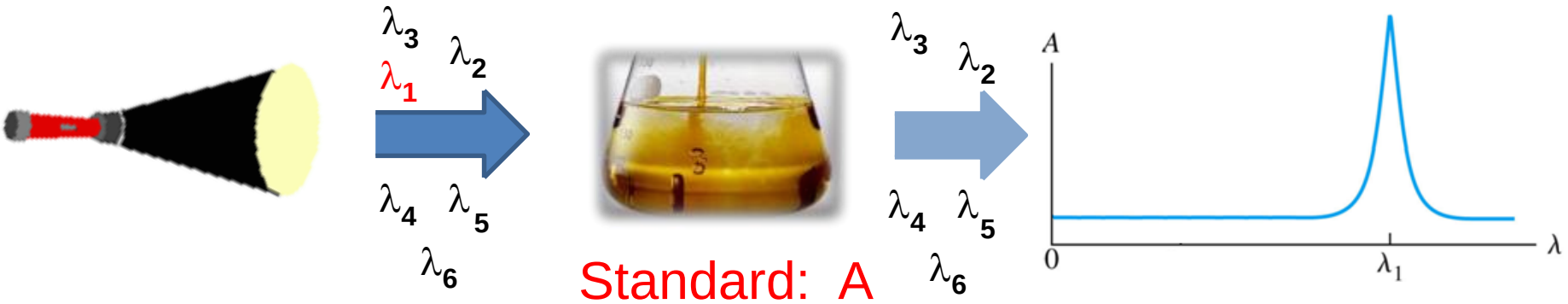
➢ Emission spectrometry (放射光譜法)



Classification of spectrometric techniques

Qualitative analysis of spectrometry:

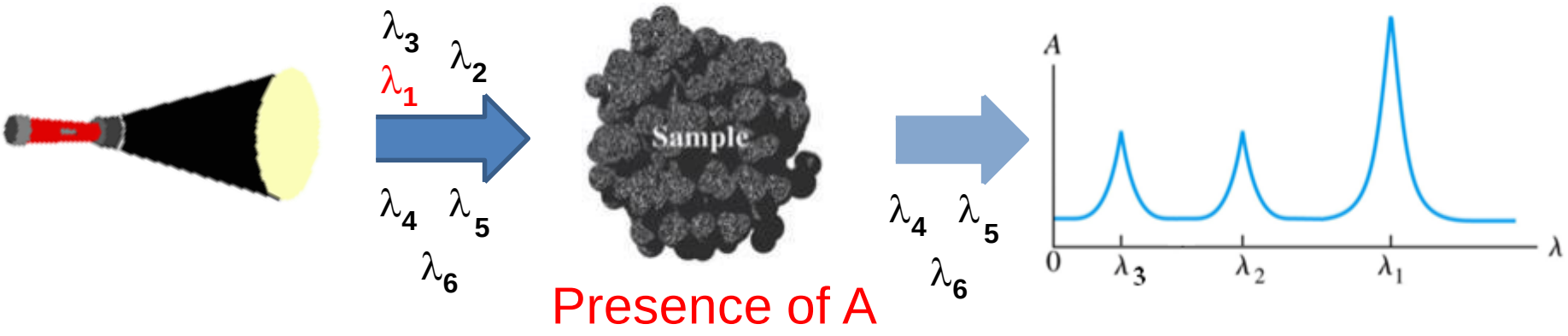
- Absorption spectrometry



Classification of spectrometric techniques

Qualitative analysis of spectrometry:

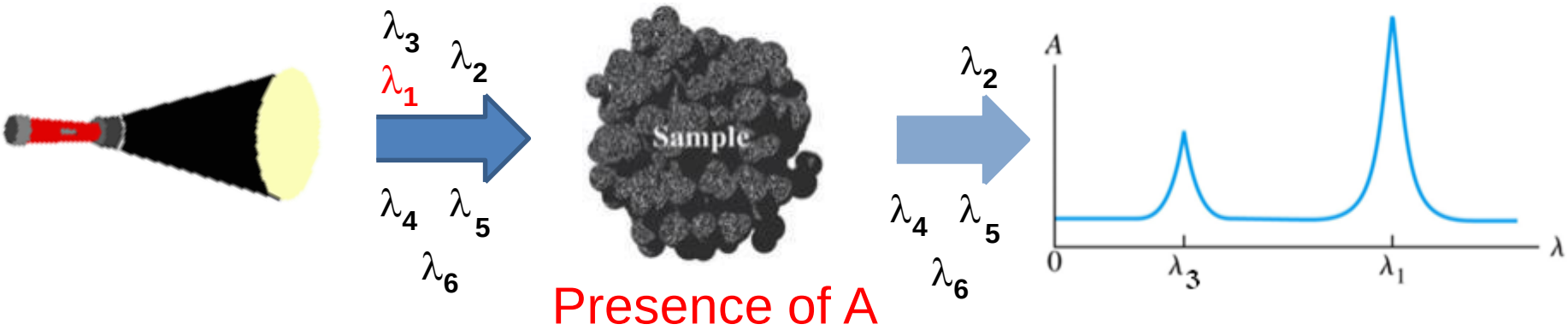
- Absorption spectrometry



Classification of spectrometric techniques

Qualitative analysis of spectrometry:

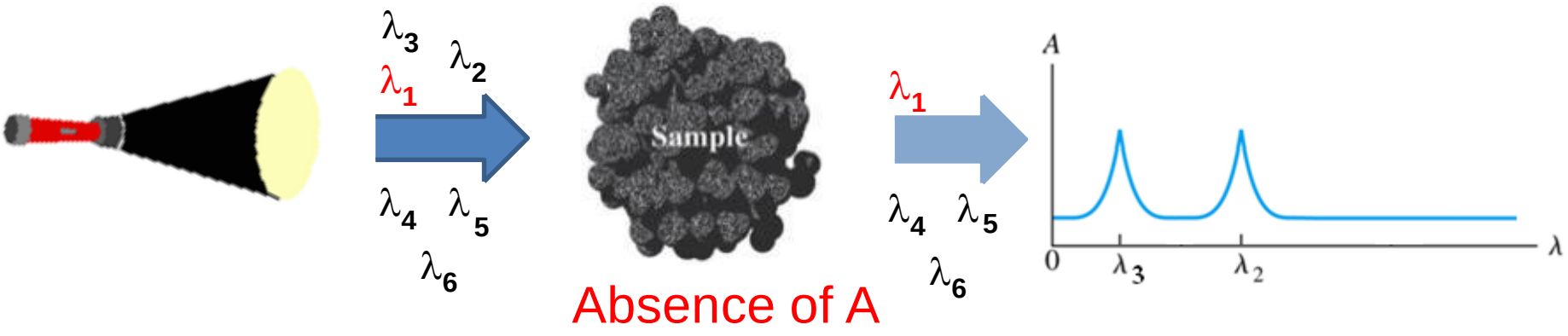
- Absorption spectrometry



Classification of spectrometric techniques

Qualitative analysis of spectrometry

- Absorption spectrometry

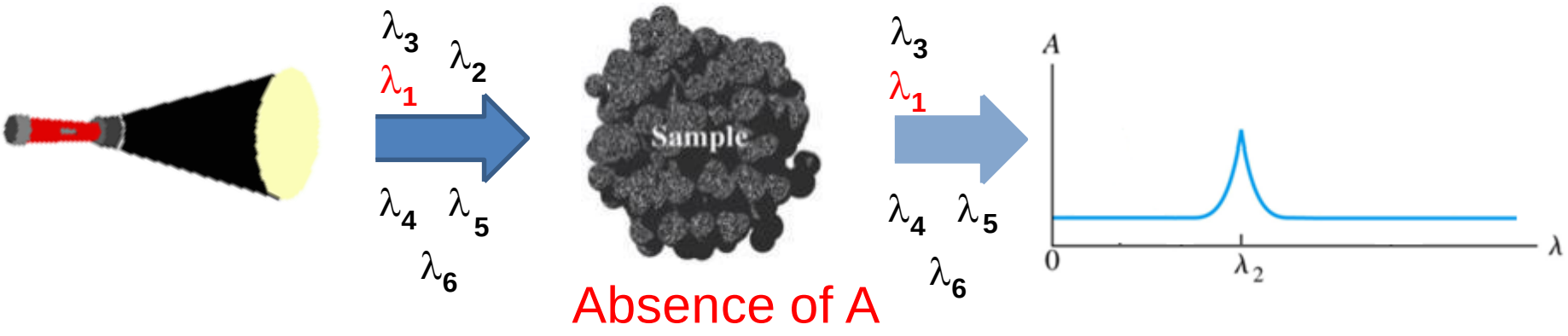


Absence of A

Classification of spectrometric techniques

Qualitative analysis of spectrometry

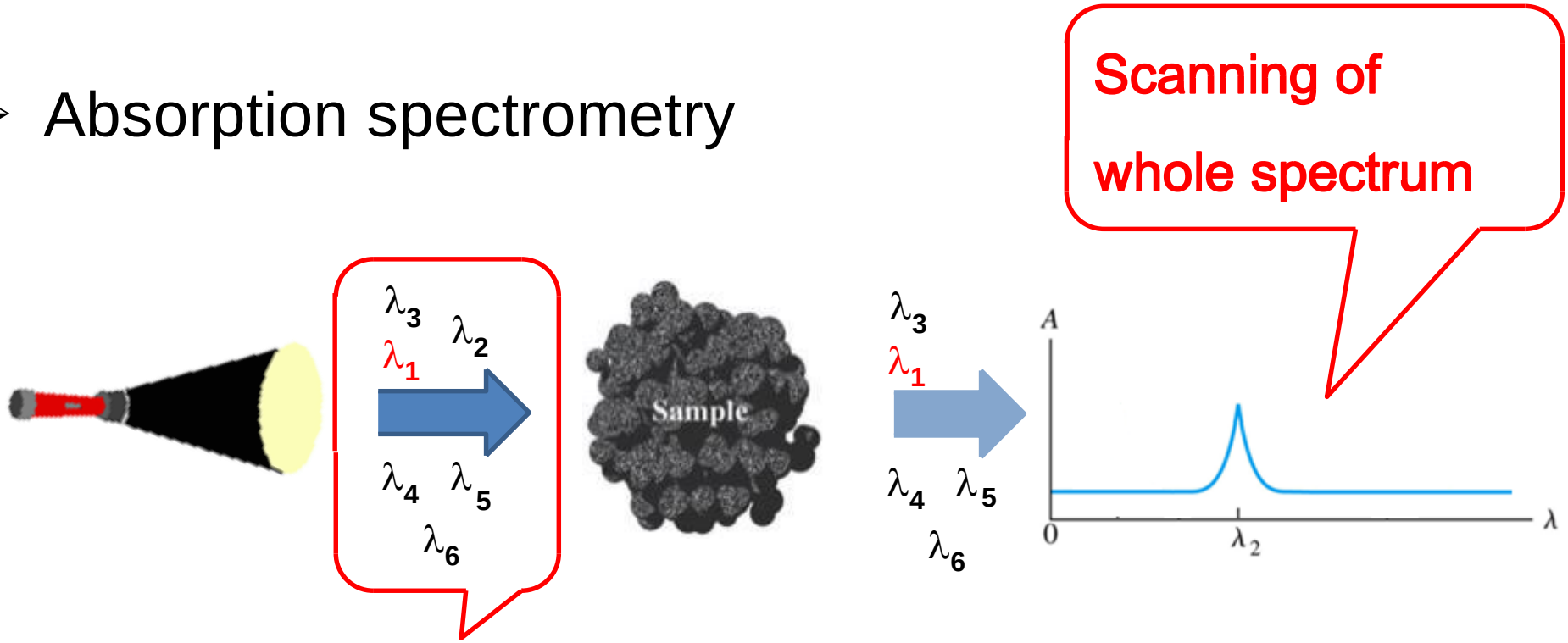
- Absorption spectrometry



Classification of spectrometric techniques

Qualitative analysis of spectrometry

- Absorption spectrometry

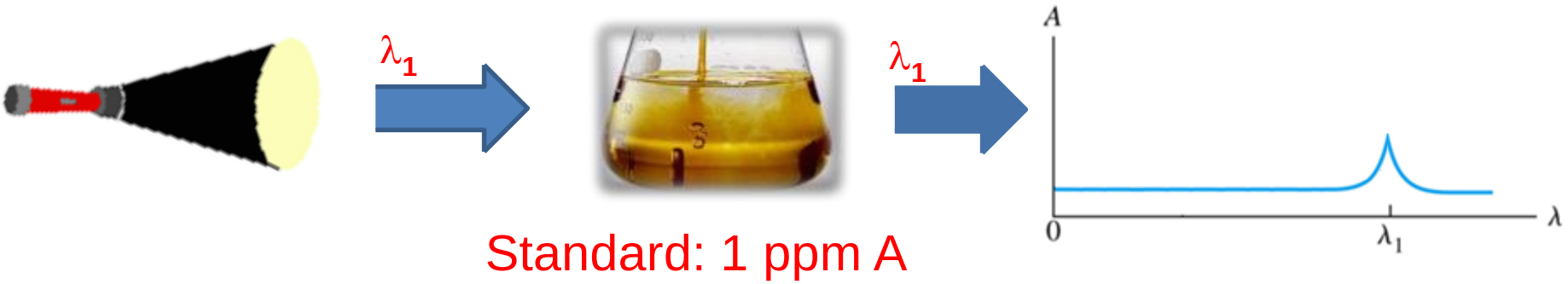


Radiation of **a range of wavelengths** on sample or standard

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- Absorption spectrometry

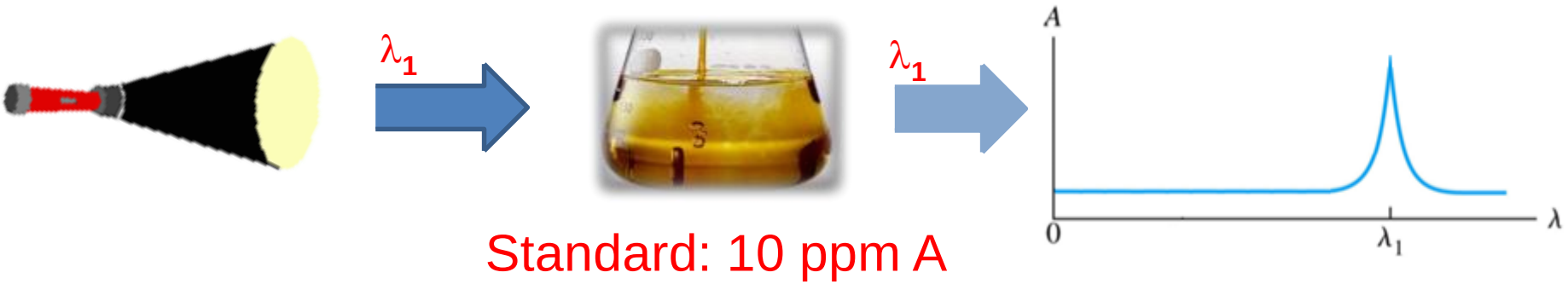


Standard: 1 ppm A

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- Absorption spectrometry

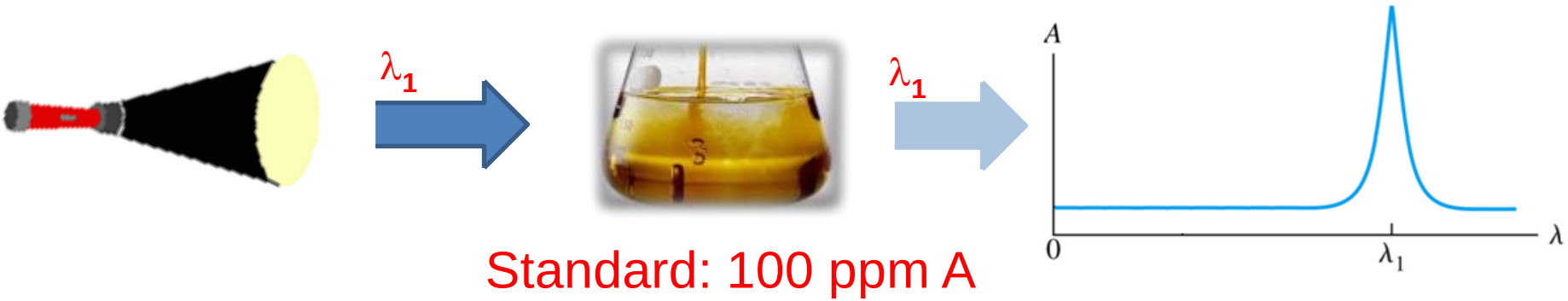


Standard: 10 ppm A

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- Absorption spectrometry

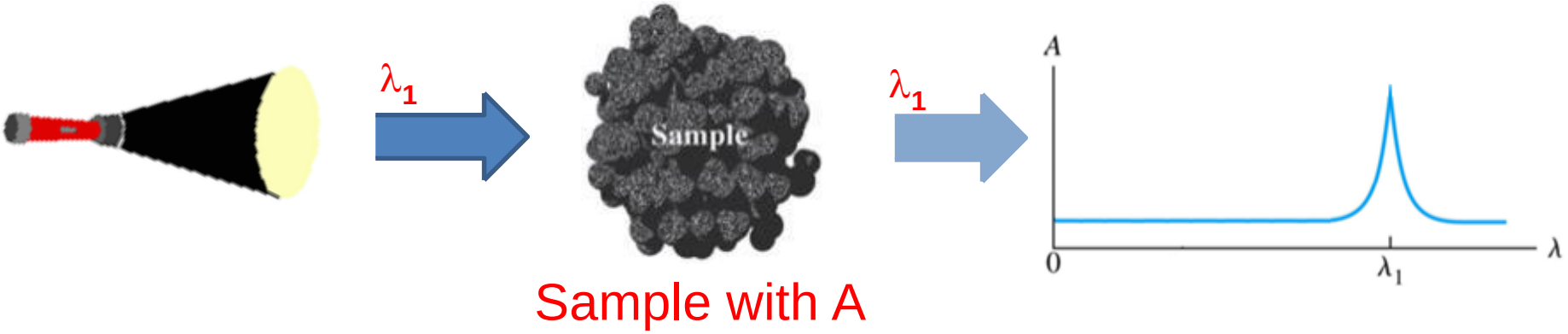


Standard: 100 ppm A

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- Absorption spectrometry



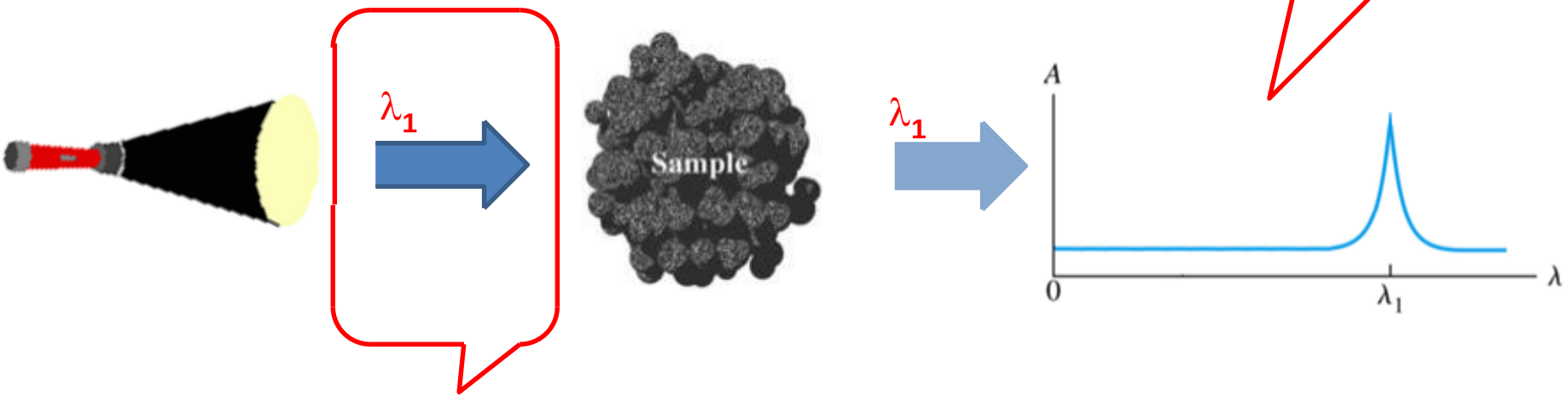
Sample with A

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- Absorption spectrometry

Use of fix wavelength

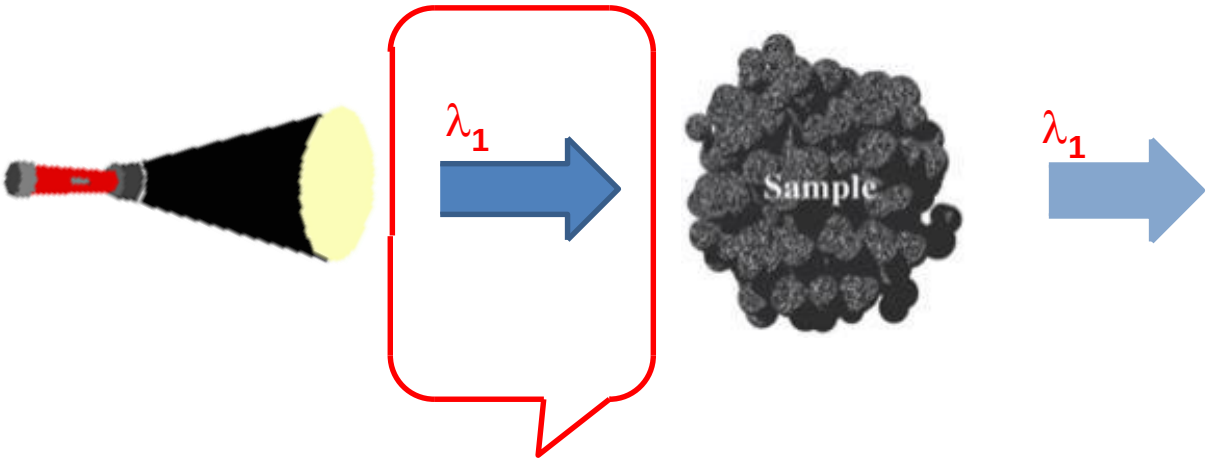


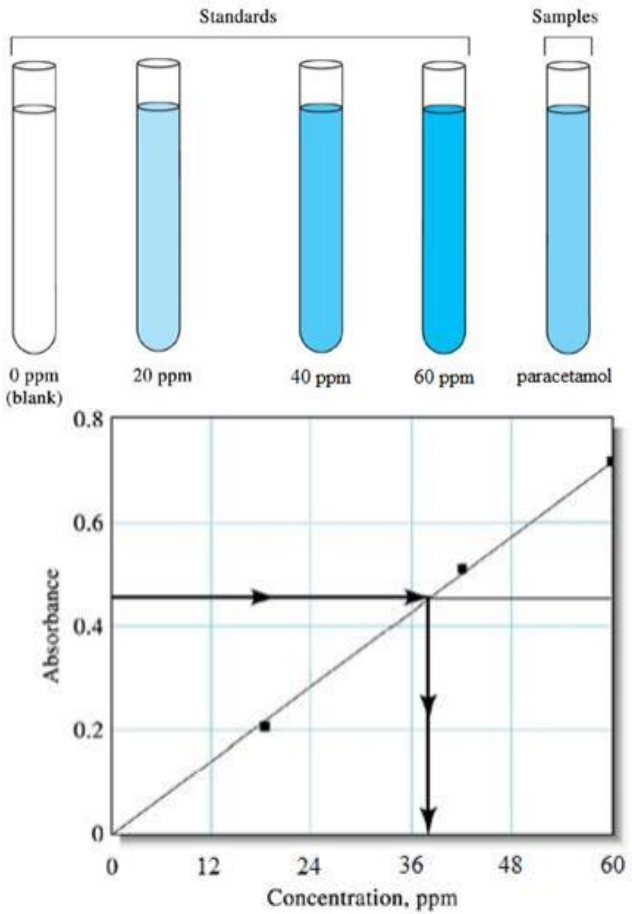
Radiation of **one wavelength** on sample or standard

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- Absorption spectrometry





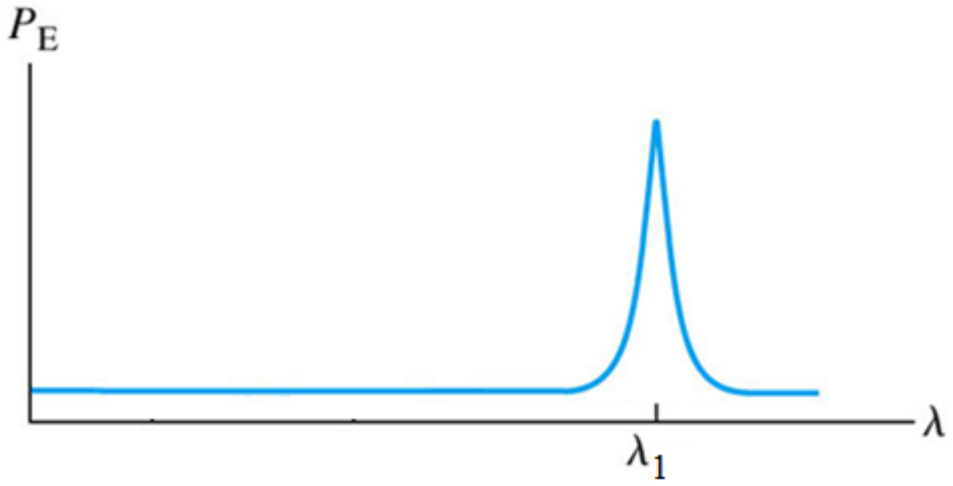
Radiation of **one wavelength** on sample or standard

Classification of spectrometric techniques

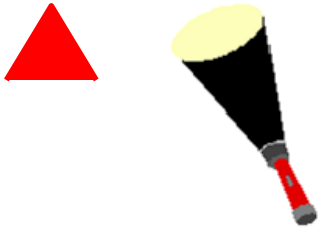
Qualitative analysis of spectrometry:

- **Emission** spectrometry

λ_1



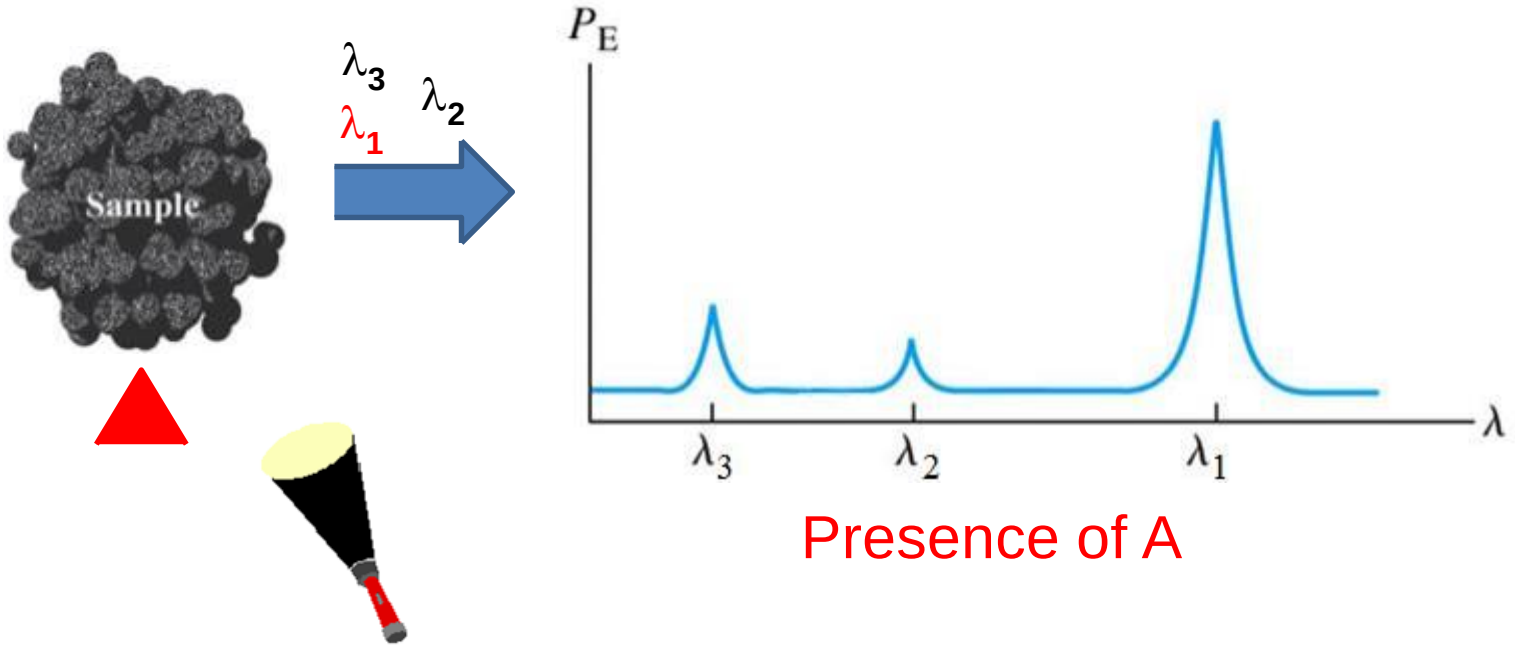
Standard: A



Classification of spectrometric techniques

Qualitative analysis of spectrometry

- **Emission** spectrometry

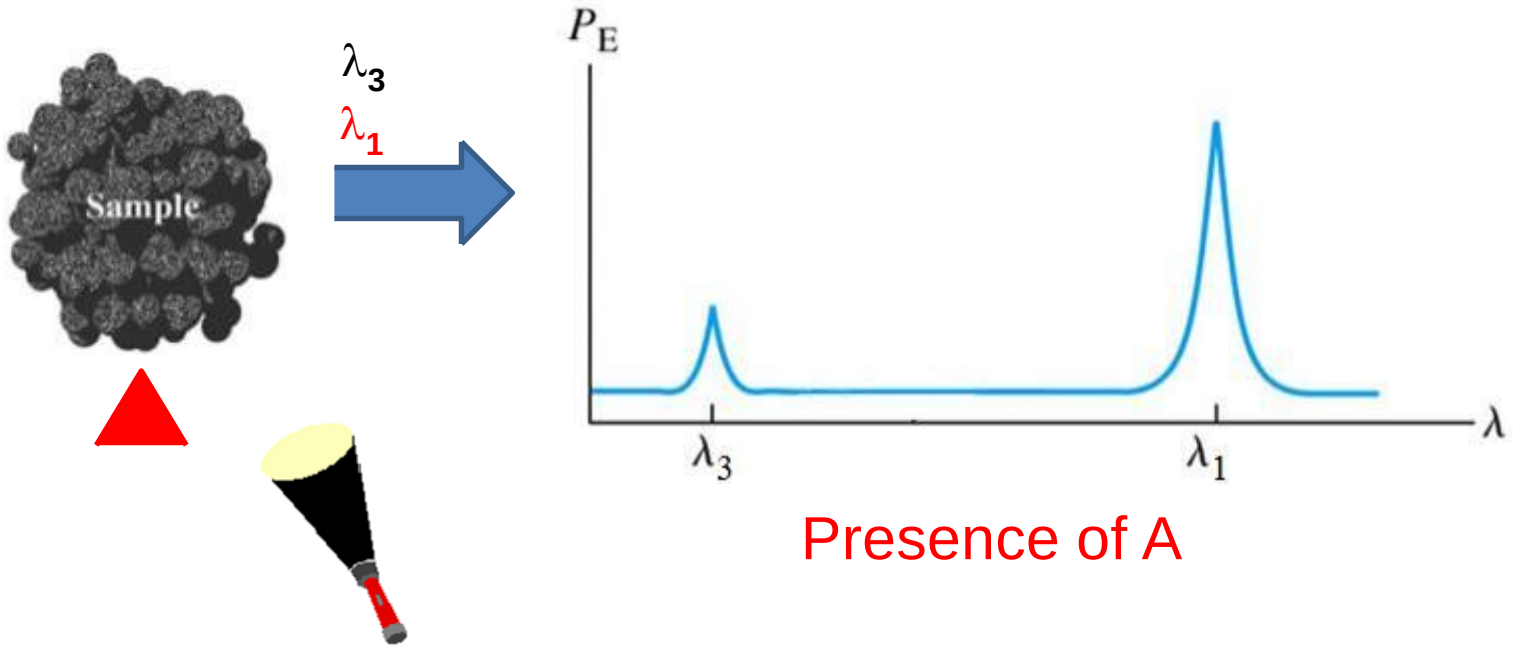


Presence of A

Classification of spectrometric techniques

Qualitative analysis of spectrometry

- **Emission** spectrometry

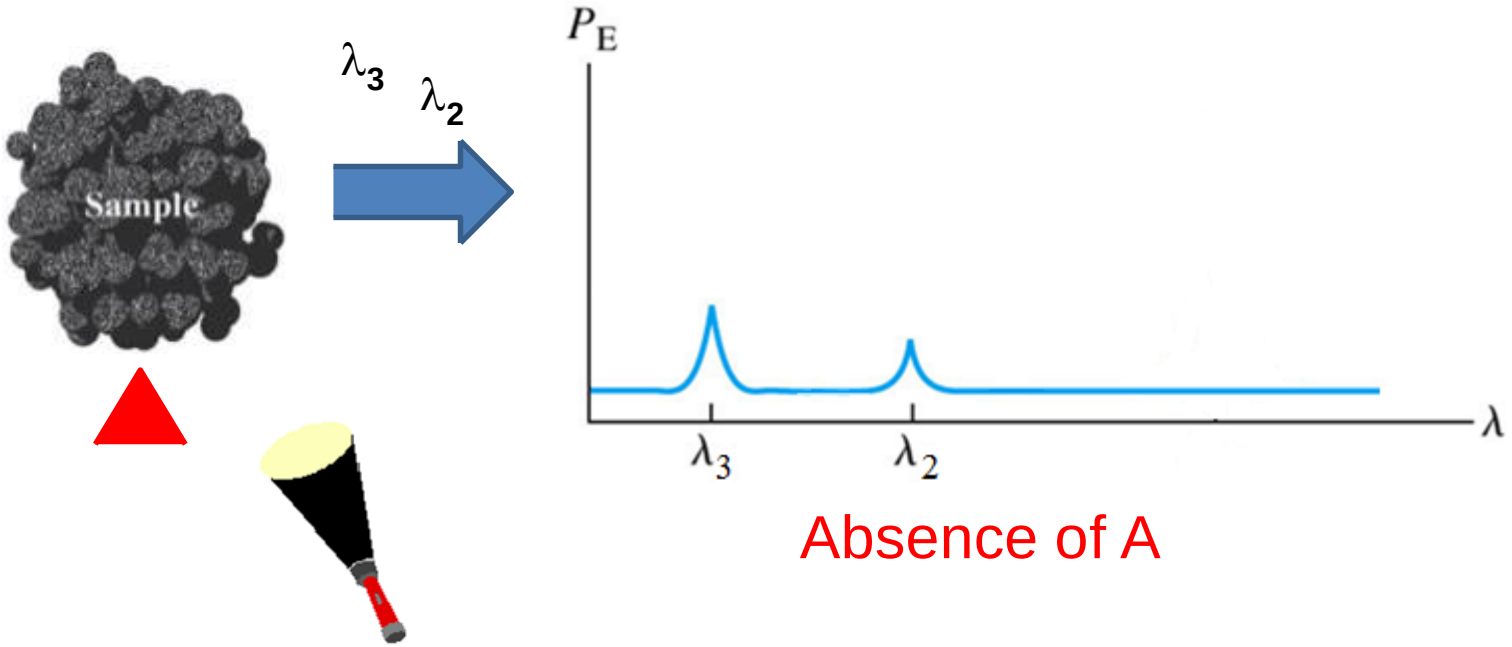


Presence of A

Classification of spectrometric techniques

Qualitative analysis of spectrometry

- **Emission** spectrometry

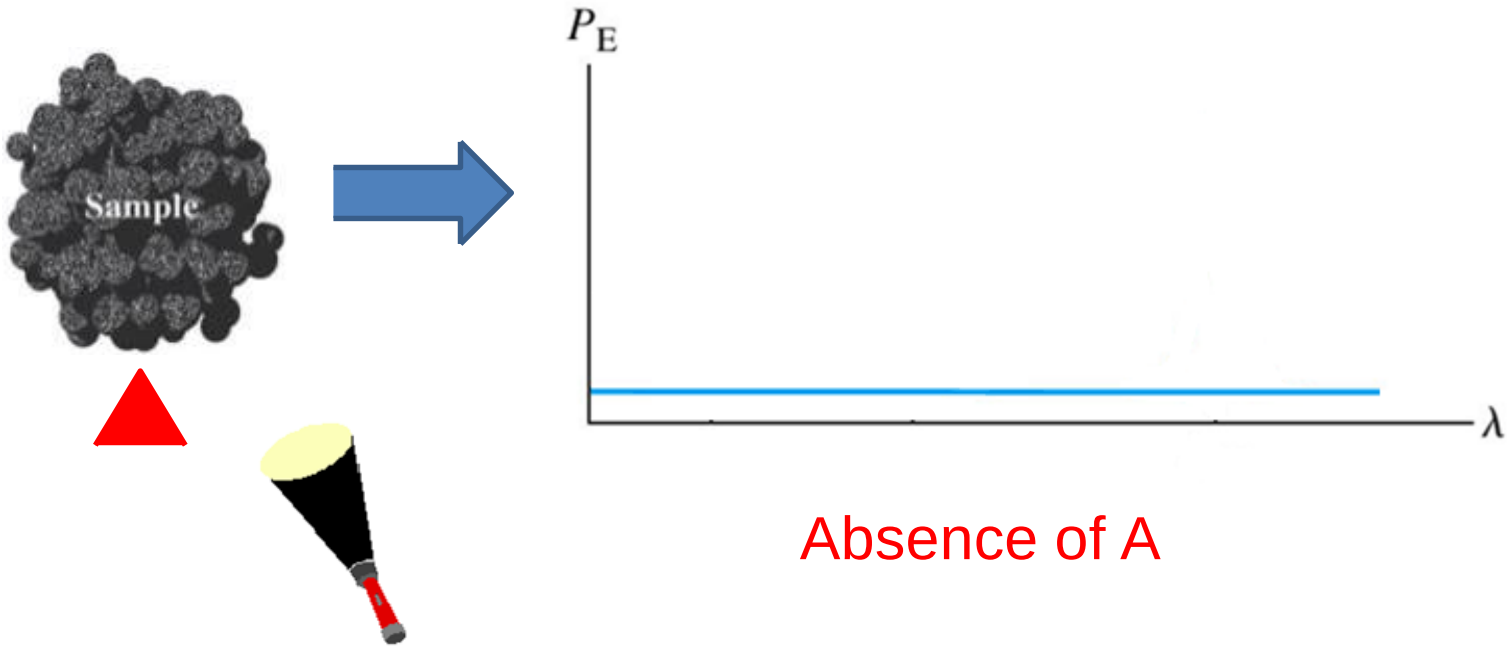


Absence of A

Classification of spectrometric techniques

Qualitative analysis of spectrometry

- **Emission** spectrometry

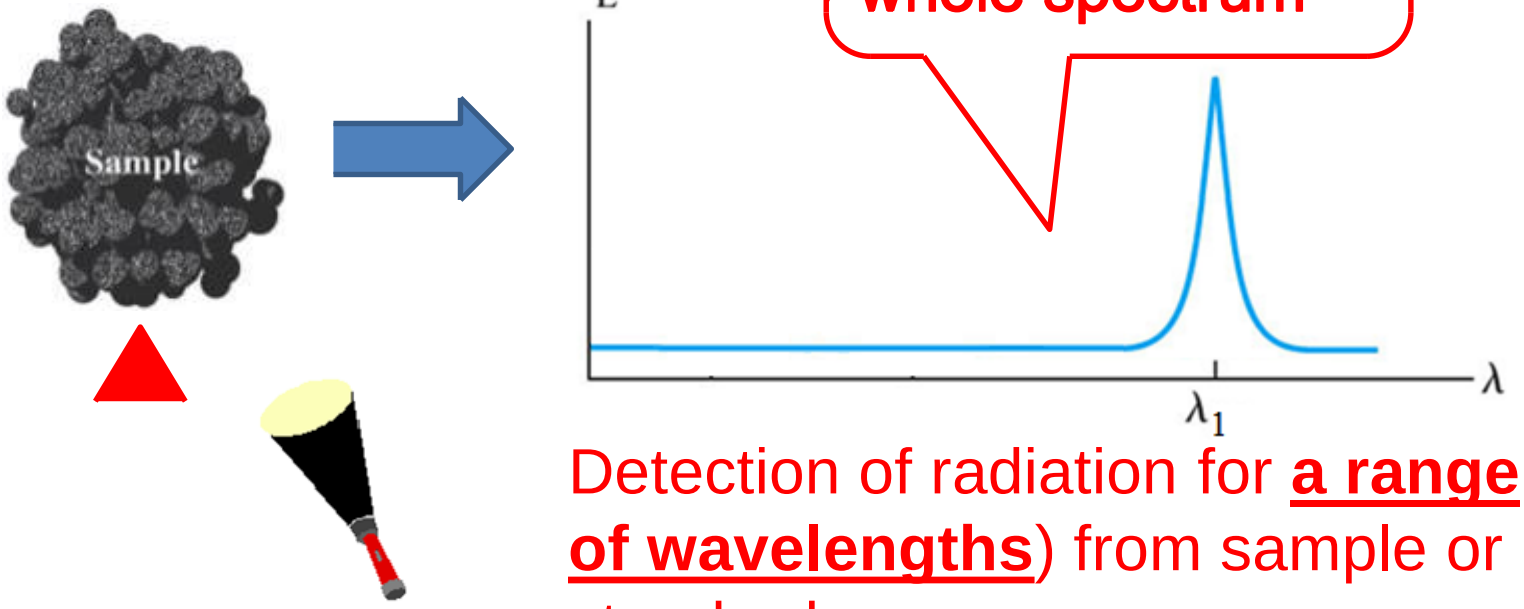


Absence of A

Classification of spectrometric techniques

Qualitative analysis of spectrometry

- **Emission** spectrometry



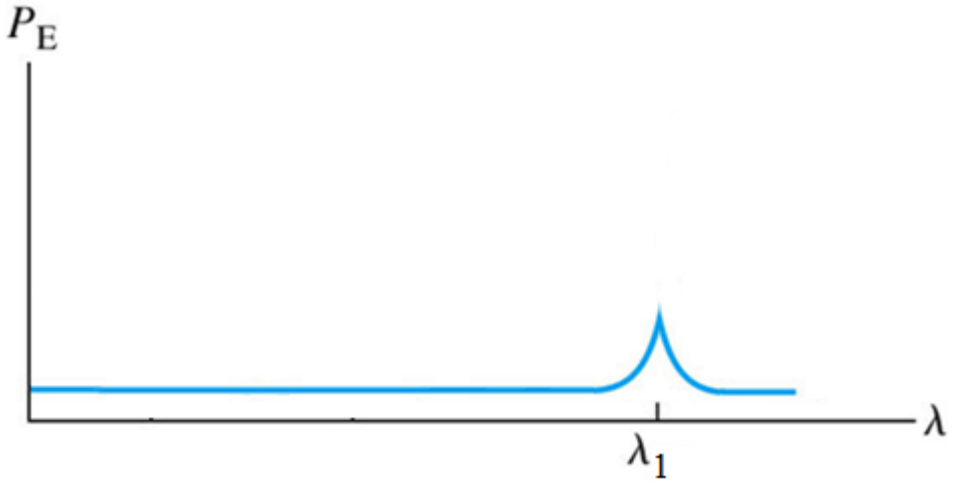
Detection of radiation for **a range of wavelengths**) from sample or standard

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- **Emission** spectrometry

λ_1



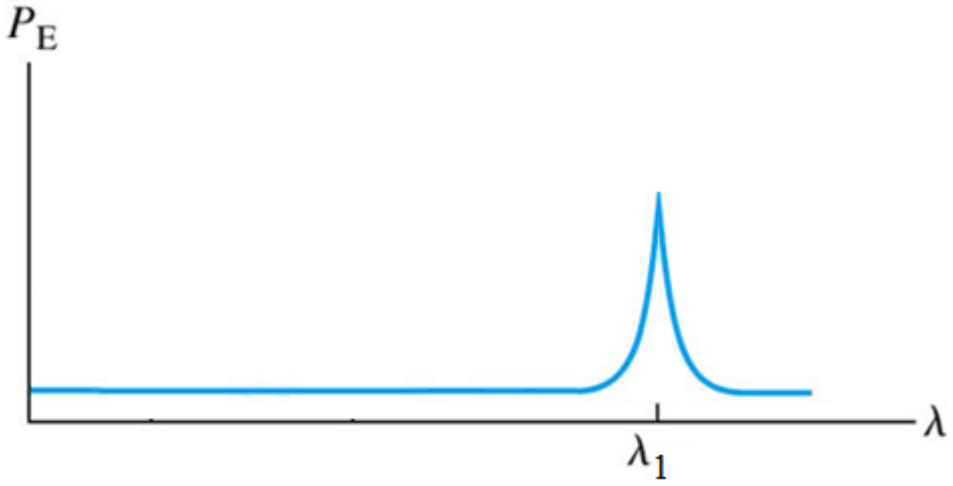
Standard: 1 ppm A

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- **Emission** spectrometry

λ_1



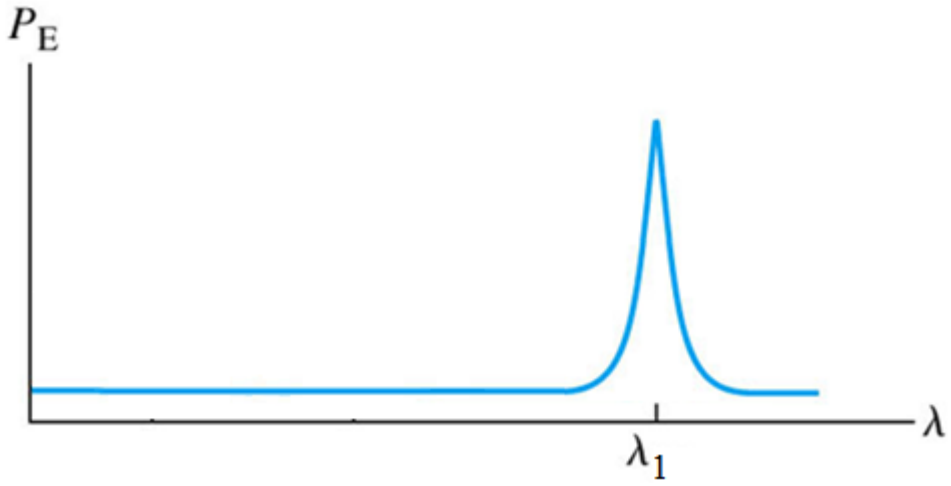
Standard: 10 ppm A

Classification of spectrometric techniques

Quantitative analysis of spectrometry

- **Emission** spectrometry

λ_1

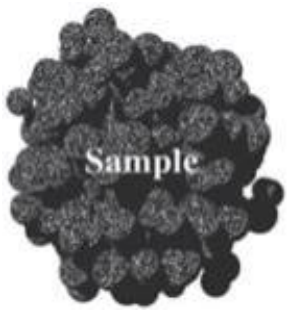


Standard: 100 ppm A

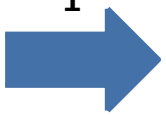
Classification of spectrometric techniques

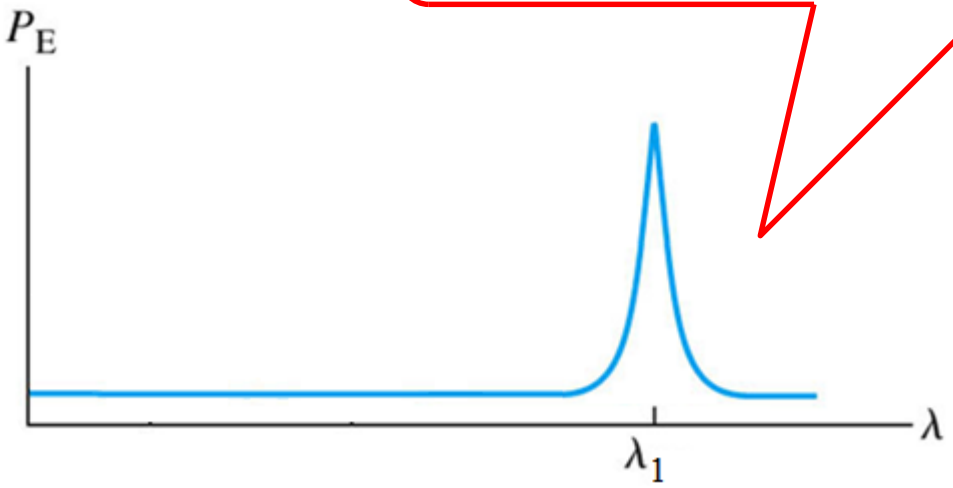
Quantitative analysis of spectrometry

- **Emission** spectrometry



Sample with A



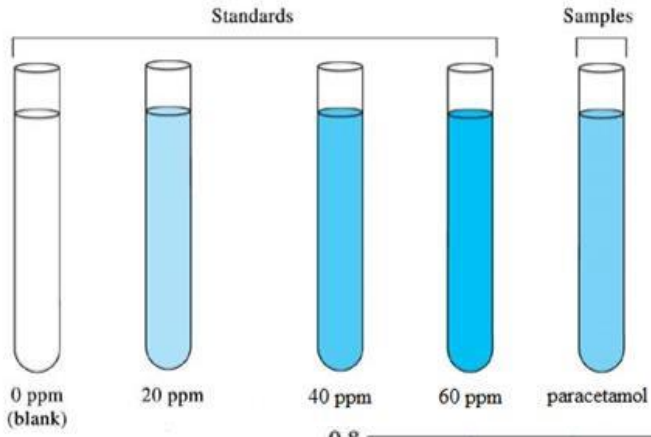


Use of fix wavelength

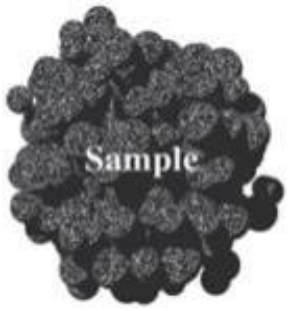
Detection of radiation (**one wavelength**) from sample or standard

Classification of spectrometric techniques

Quantitative analysis of spectrometry



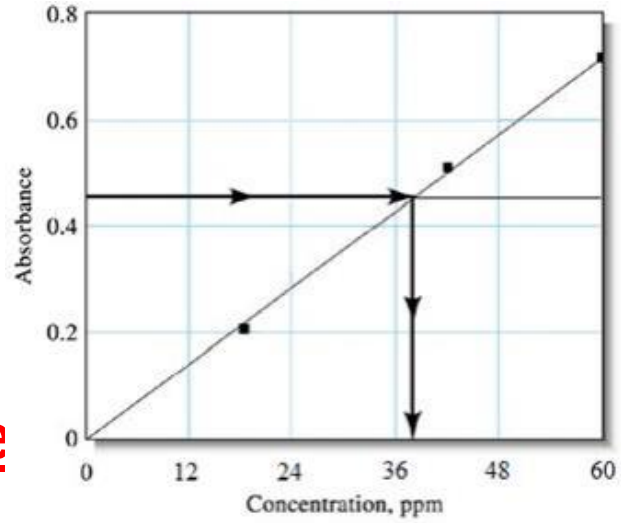
- **Emission** spectrometry



λ_1

Sample with A

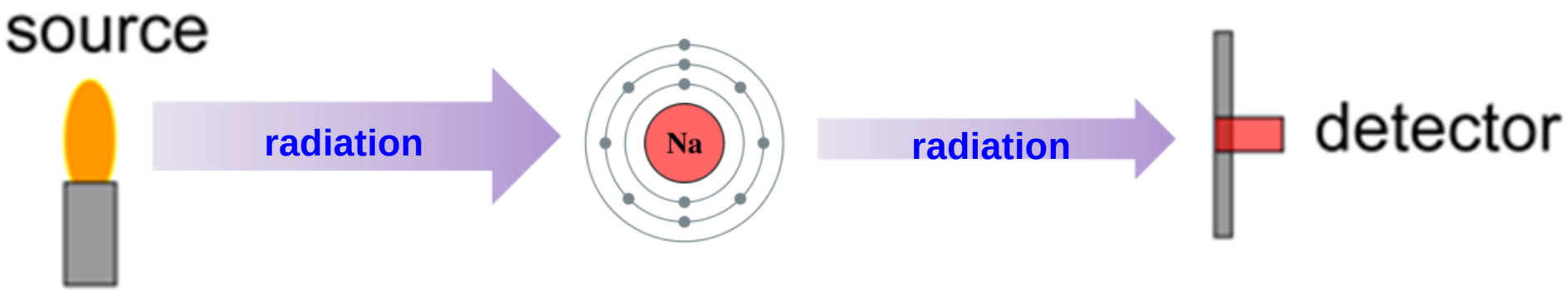
Detection of radiation (**one wavelength**) from sample or standard



Classification of spectrometric techniques

- Atomic spectroscopy (原子光譜學):

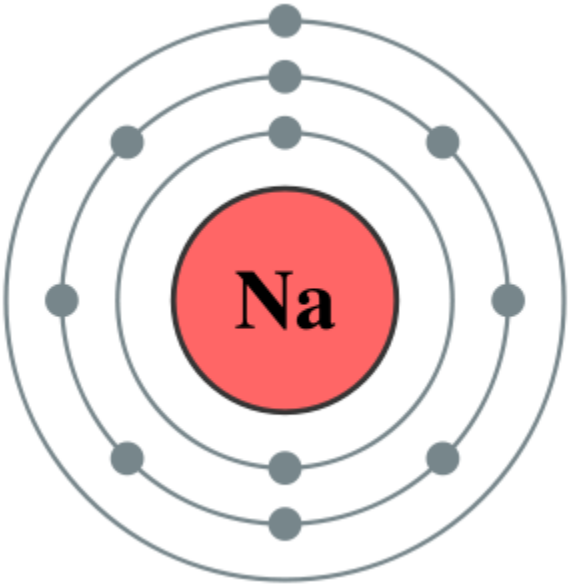
➢ a study of the interactions of radiation with atoms

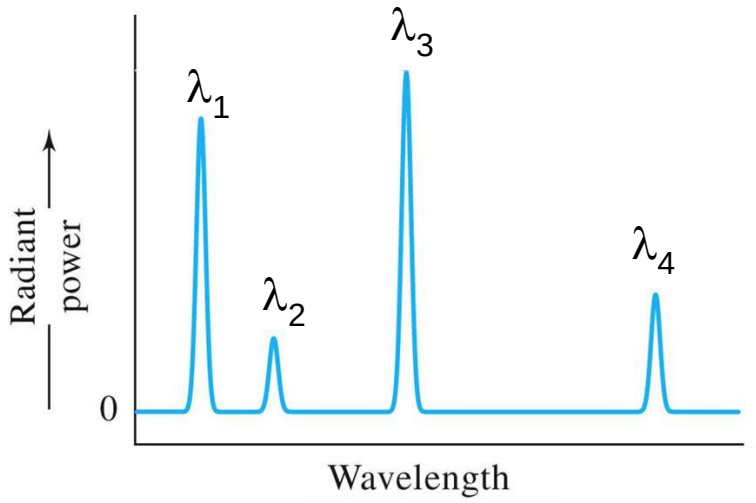


Classification of spectrometric techniques

- Atomic spectroscopy (原子光譜學):

➢ a study of the interactions of radiation with atoms



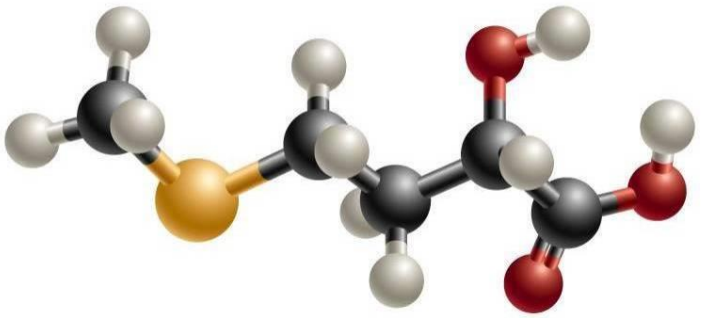


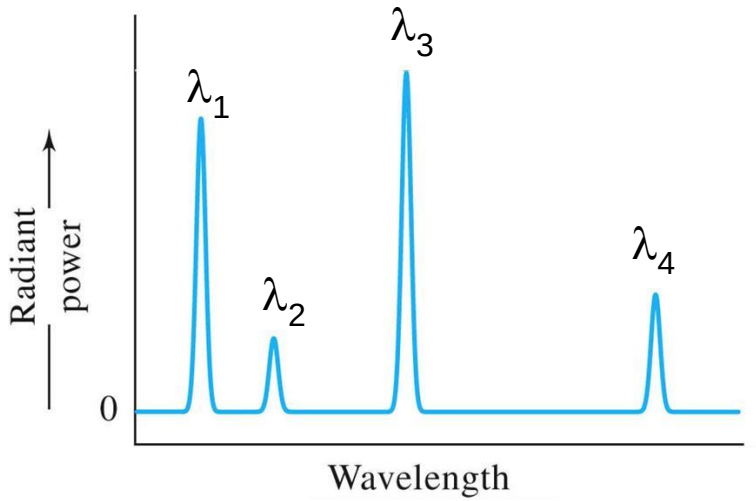
line spectrum (線光譜)

Classification of spectrometric techniques

- Atomic spectroscopy (原子光譜學):

➢ a study of the interactions of radiation with atoms



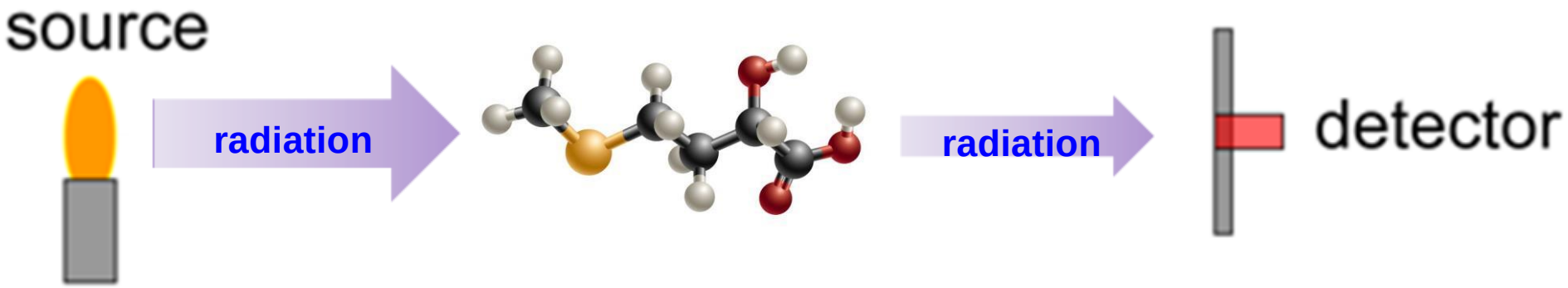


line spectrum (線光譜)

Classification of spectrometric techniques

- Molecular spectroscopy (分子光譜學):

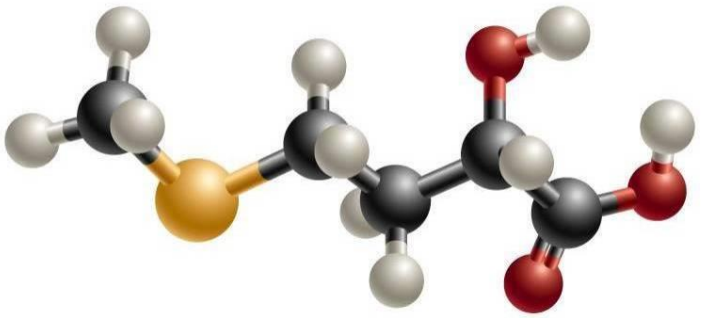
➢ a study of the interactions of radiation with molecules

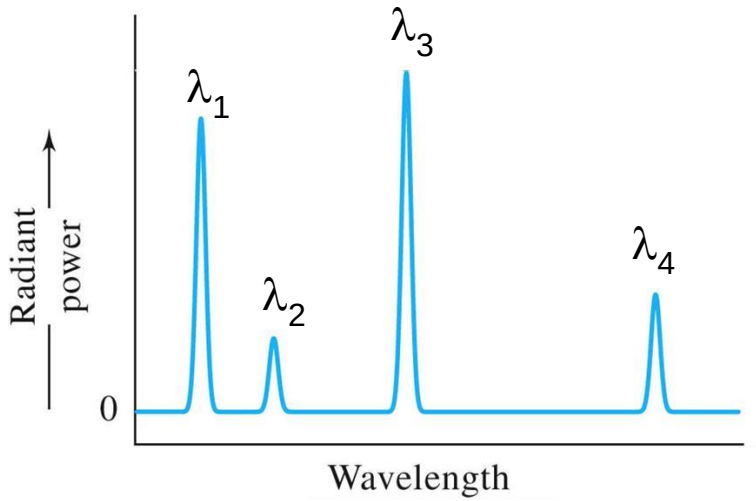


Classification of spectrometric techniques

- Molecular spectroscopy (分子光譜學):

➢ a study of the interactions of radiation with molecules



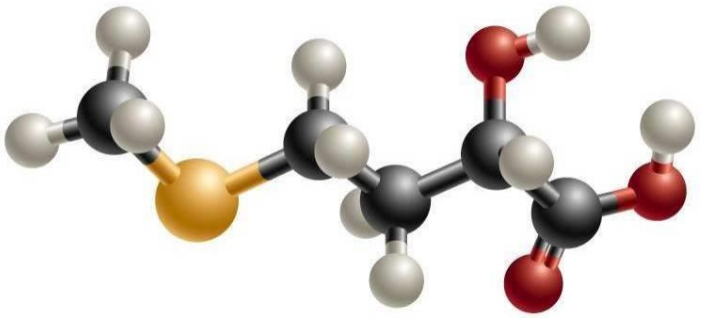


line spectrum (線光譜)

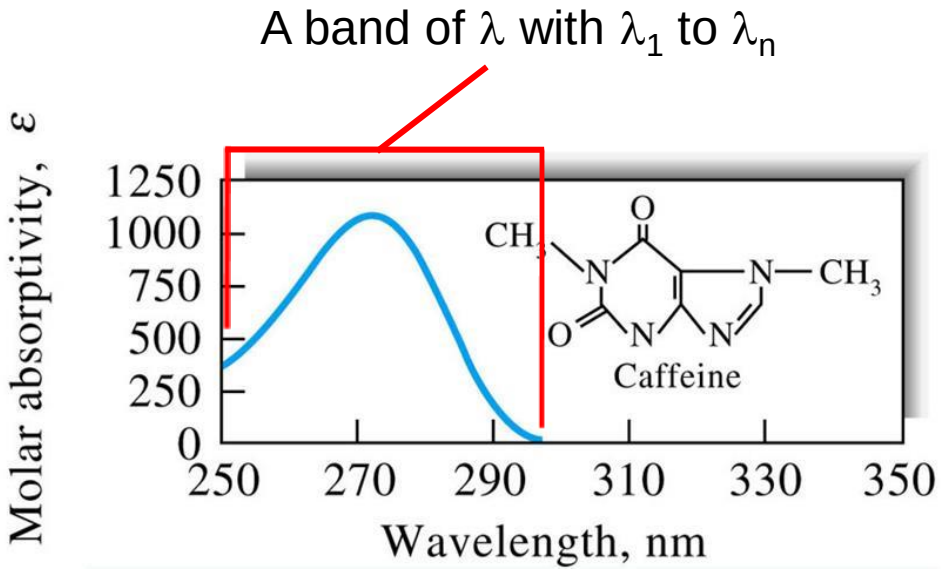
Classification of spectrometric techniques

- Molecular spectroscopy (分子光譜學):

➢ a study of the interactions of radiation with molecules



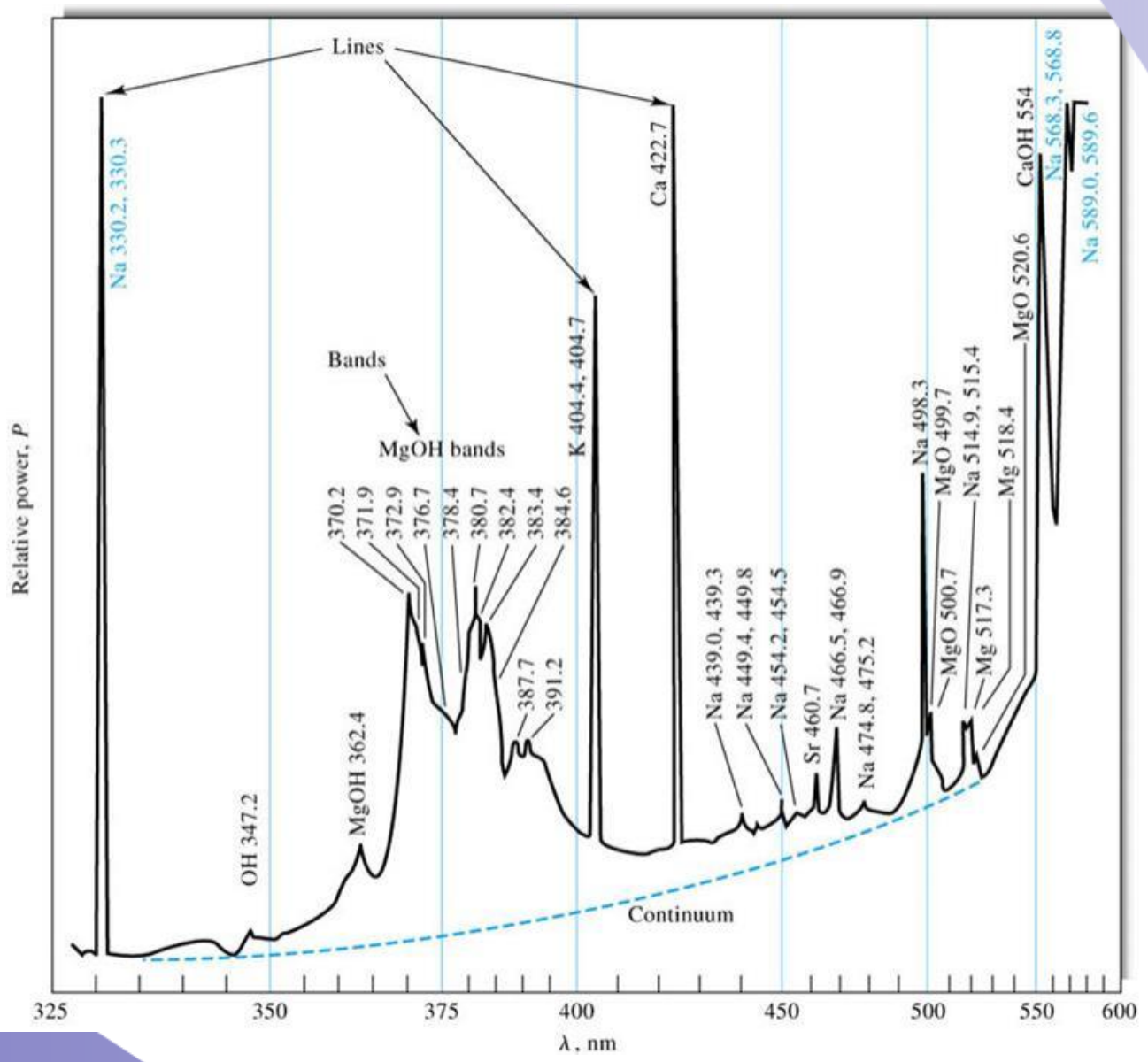
Why does band spectrum happen?



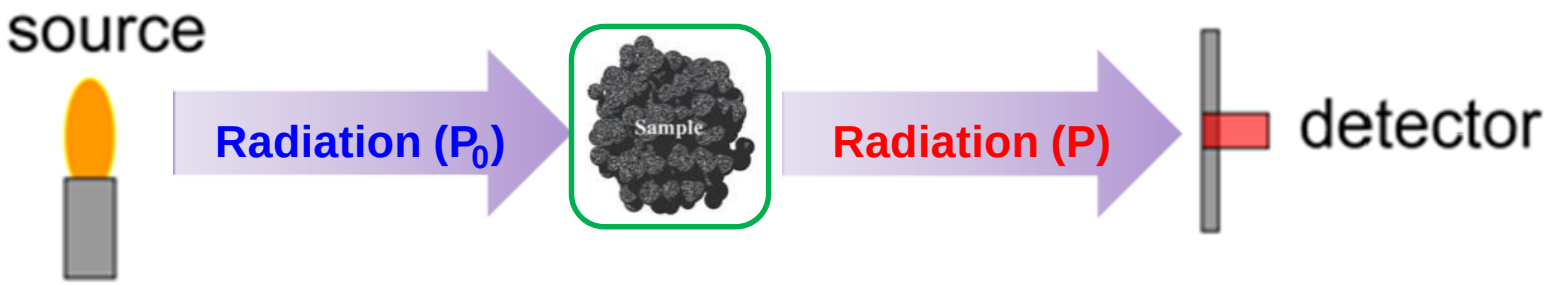
band spectrum (帶光譜)

Classification of spectrometric techniques

band spectrum (帶光譜)



- For quantitative analysis using absorption methods, concentration of standards or unknown samples is related to the ratio of the radiant power of the transmitted (傳達) beam (P) to that of the radiant power of the incident beam (P_0)



Absorption spectrometry

- For quantitative analysis using absorption methods,

Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, P_e	$P_e = kc$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Absorption	Incident, P_0, and transmitted, P	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

- For quantitative analysis using absorption methods,

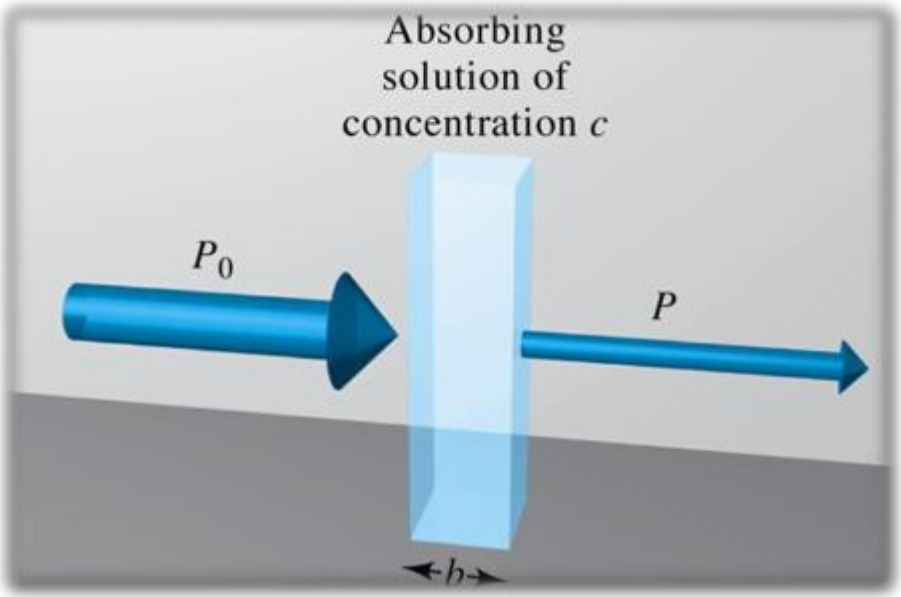
Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, P_e	$P_e = kc$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Absorption	Incident, P_0, and transmitted, P	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

Relationship between A, P/P_0 and c

- For quantitative analysis using absorption methods,

➢ **Absorbance (吸收率)**

$A = \log (P_0/P)$



- For quantitative analysis using absorption methods,

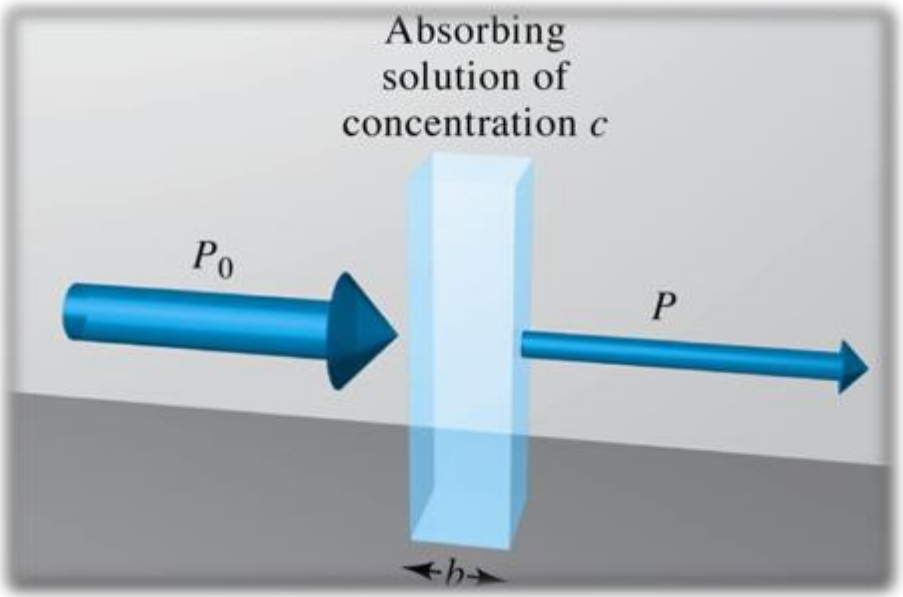
➢ **Beer's law (比爾定律)**

$A \propto b \propto c$

$A = abc = \varepsilon bc = \log (P_0/P)$

a = absorptivity (吸收性)

ε = molar absorptivity (莫耳吸光係數)



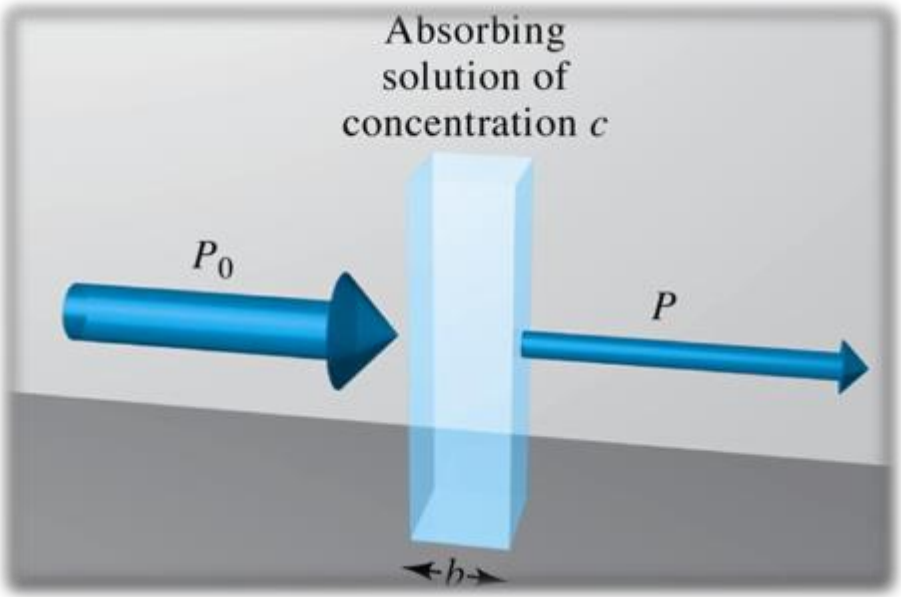
- For quantitative analysis using absorption methods,

➢ **Absorbance (吸收率)**

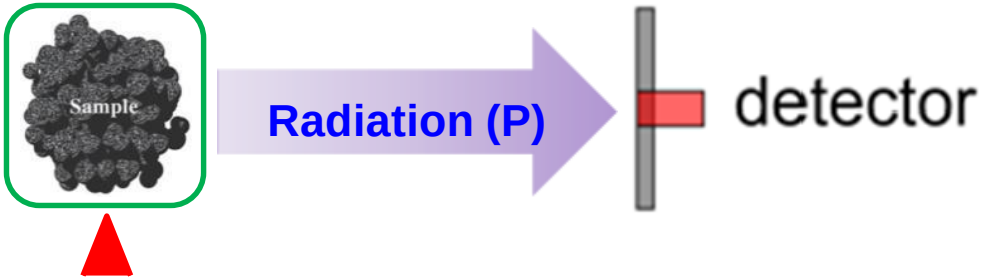
$A = \log (P_0/P) = -\log_{10} T$

➢ **Transmittance (透光率)**

$T\ \% = P / P_0 \times 100\%$



- For quantitative analysis using emission methods, concentration of standards or unknown samples $\propto$ emitted radiant power (P)

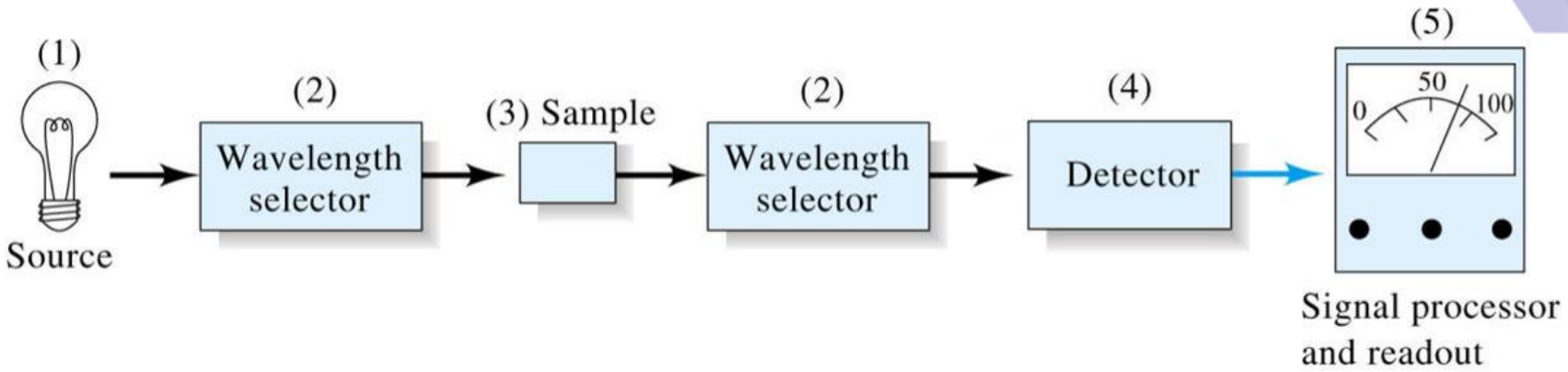


Emission spectrometry

- For quantitative analysis using emission methods,

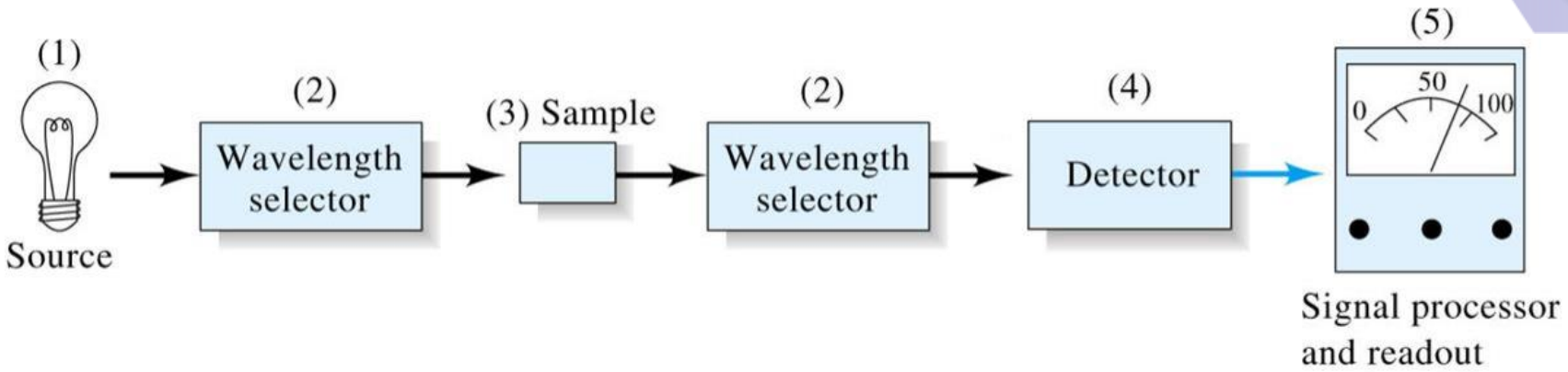
Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, P_e	$P_e = kc$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Absorption	Incident, P_0, and transmitted, P	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

Components of optical instruments



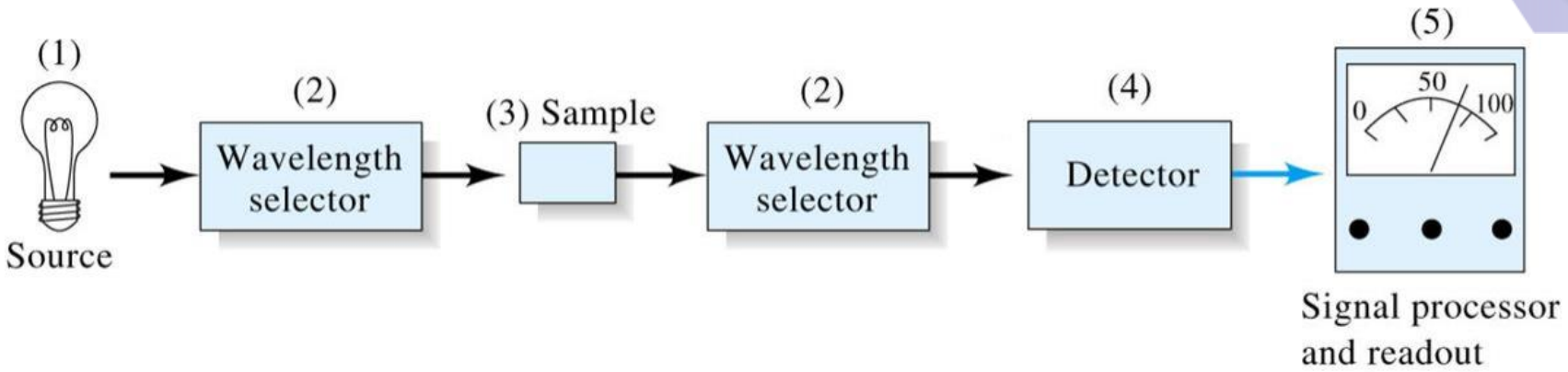
Flame atomic absorption spectrometer (FAAS)

Components of optical instruments



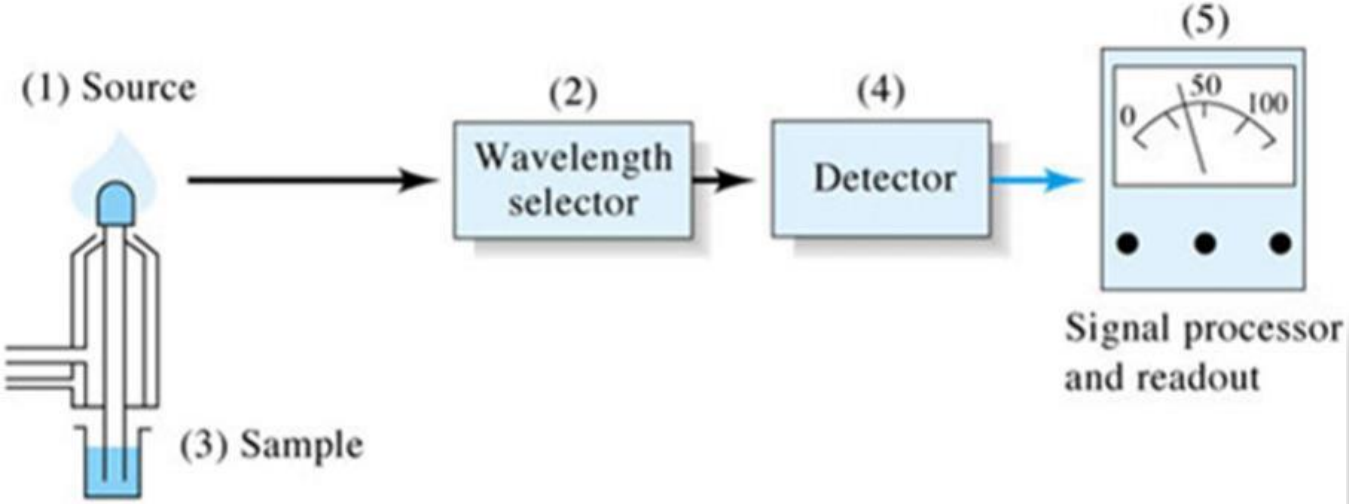
Ultraviolet / visible spectrophotometer

Components of optical instruments



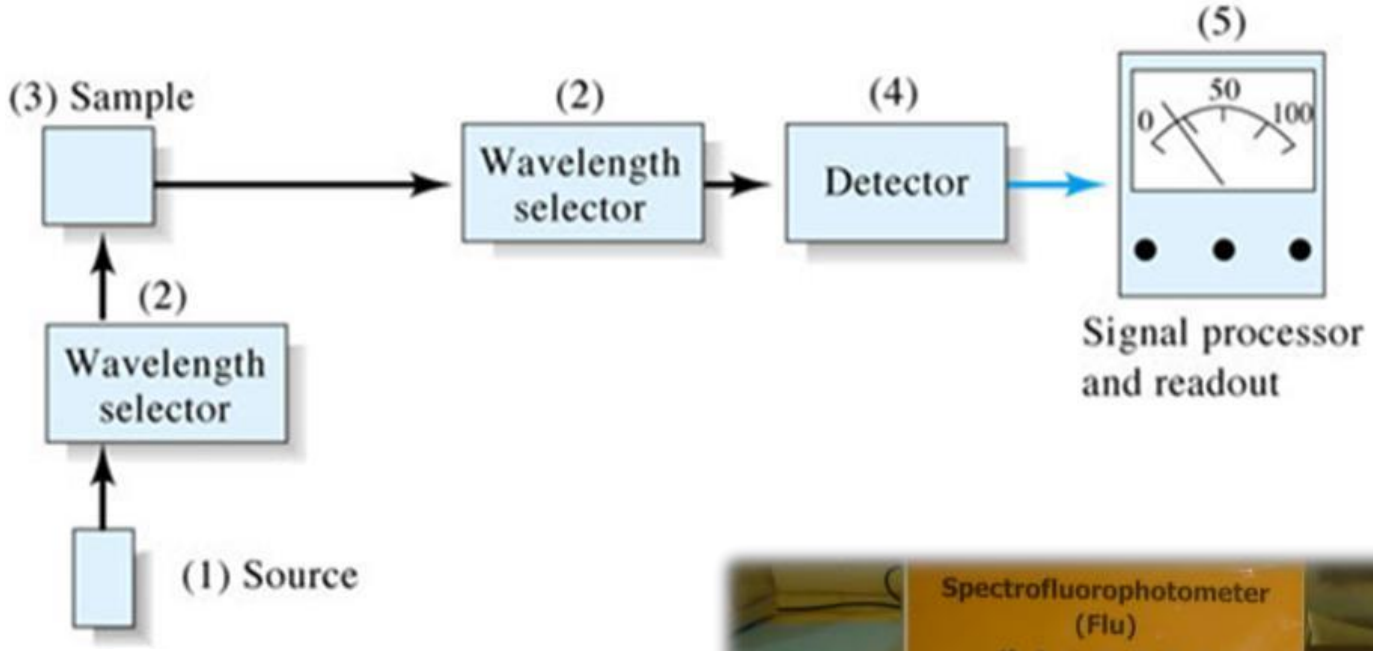
Fourier Transform infrared spectrometer (FT-IR)

Components of optical instruments



Flame photometer (flame emission spectrometer)

Components of optical instruments



Spectrofluorophotometer

Wave–particle duality(波粒二象性)

Wave–particle duality is the concept in quantum mechanics that every particle or quantic entity may be partly described in terms not only of particles, but also of waves. It expresses the inability of the classical concepts "particle" or "wave" to fully describe the behavior of quantum-scale objects. As Albert Einstein wrote:[1]

It seems as though we must use sometimes the one theory and sometimes the other, while at times we may use either. We are faced with a new kind of difficulty. We have two contradictory pictures of reality; separately neither of them fully explains the phenomena of light, but together they do.